

### REMARKS/ARGUMENTS

Reconsideration of this application is requested. Claims 1-21 and 31-36 remain active in the application subsequent to entry of this Amendment.

In the instructions given above, claims 22-30 have been canceled in order to resolve the issues and rejections stated in item 2 of the Official Action.

This leaves for consideration the rejections stated in items 3 and 4 of the Official Action directed to claims 1-21 and 31-36. The primary reference is published European application EP 0957474 A1 to Hayashi et al which has a publication date of November 17, 1999. Applicants claim benefit of two prior Japanese applications dated November 15 and November 16, 1999, both before the publication date of the reference cited and relied upon.

In the Amendment and response filed April 24, 2003 I submitted English translations of these two documents; see the discussion in the last paragraph of page 20 of the Remarks as well as the attached photocopy of a postcard receipt bearing the USPTO mailroom date stamp of April 24, 2003 and indicating translations were submitted. It is counsel's belief that these translations became disassociated with the April 24, 2003 Amendment during initial processing and thus were not in the examiner's hands at the time the current Official Action was prepared.

To facilitate further consideration attached are additional copies of the translations, including verifications, for the examiner's convenience. If, for some reason, these translations do not reach the examiner's hands with this response, please contact the undersigned by telephone and I will arrange for an in-person delivery of these documents.

As applicants' claim for benefit of priority under 35 USC §119 has been perfected and a day prior to the day of publication of the cited European patent 0957474 has been established, this citation is no longer available as prior art and the rejections stated in items 3 and 4 of the Official Action must be withdrawn. These rejections being

HAYASHI et al  
Appl. No. 09/710,834  
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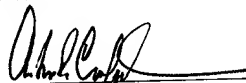
withdrawn, there are no further issues for consideration and claims 1-21 and 31-36 should be allowed.

Concurrently with this response the undersigned is filing a Notice of Appeal in order to maintain pendency of this application.

Respectfully submitted,

**NIXON & VANDERHYE P.C.**

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VERIFICATION OF A TRANSLATION

I, the below named translator, hereby declare that:

That my name is Toshisada YAMAMURO;

That my address is 170, Mamashita, Minamiashigara-shi,  
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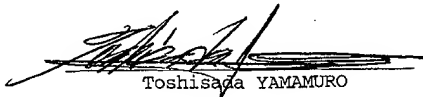
That I know well both the English and Japanese  
languages;

That I translated a Certified Copy of Japanese Patent  
Application No. 11-324150 filed on November 15, 1999,  
into the English language;

That the attached English language translation is a true  
and correct translation of the Certified Copy of  
Japanese Patent Application No. 11-324150 filed on  
November 15, 1999, to the best of my knowledge and  
belief; and

That I hereby declare that all statements made herein of  
my own knowledge are true and that all statements made  
on information and belief are believed to be true; and  
further that these statements were made with the  
knowledge that willful false statements and the like so  
made are punishable by fine or imprisonment, or both,  
under section 1001 of Title 18 of the United States Code  
and that such willful false statements may jeopardize  
the validity of the application or any patent issued  
thereon.

Date: December 19, 2003

  
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DOCUMENT NAME: Patent Application  
REFERENCE NUMBER: F 964  
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INDICATION OF FEE:

NUMBER OF PAYMENT-IN-ADVANCE BOOK: 001029

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LIST OF OBJECTS SUBMITTED:

OBJECT NAME: Specification 1

OBJECT NAME: Abstract 1

PROOF: Required

DOCUMENT NAME: SPECIFICATION

TITLE OF THE INVENTION

MAGNETIC ACICULAR PARTICLES FOR MAGNETIC RECORDING  
MEDIUM AND MAGNETIC RECORDING MEDIUM USING  
THE SAME

WHAT IS CLAIMED IS:

1. Magnetic acicular particles for a magnetic recording medium, comprising black magnetic acicular composite particles having an average particle diameter of 0.051 to 0.35  $\mu\text{m}$  and an absorption amount of myristic acid of 0.01 to 0.3  $\text{mg}/\text{m}^2$ , and comprising:

as core particles, magnetic acicular cobalt-coated iron oxide particles or magnetic acicular metal particles containing iron as a main component,

a coating formed on surface of said core particles, comprising: (1) organosilane compounds obtainable from alkoxy silane compounds, or (2) polysiloxanes, and

a carbon black adhered on at least a part of said coating in an amount of from more than 10 to 40 parts by weight based on 100 parts by weight of the core particles.

2. Magnetic acicular particles for a magnetic recording medium, comprising black magnetic acicular composite particles having an average particle diameter of 0.051 to 0.35  $\mu\text{m}$  and an absorption amount of myristic acid of 0.01 to 0.3  $\text{mg}/\text{m}^2$ , and comprising:

magnetic acicular cobalt-coated iron oxide particles or magnetic acicular metal particles containing iron as a main component,

as a lower layer, a coat formed on the surface of said magnetic acicular cobalt-coated iron oxide particles or magnetic acicular metal particles containing iron as a main component, comprising at least one compound selected from the group consisting of hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon

a coating formed on the lower layer, comprising organosilane compounds obtainable from alkoxysilane compounds, or polysiloxanes, and

a carbon black adhered on at least a part of said coating in an amount of from more than 10 to 40 parts by weight based on 100 parts by weight of the core particles.

3. A magnetic recording medium comprising:

a non-magnetic base film; and

a magnetic recording layer comprising a binder resin and as magnetic particles, magnetic acicular particles as defined in claim 1 or 2.

#### DETAILED DESCRIPTION OF THE INVENTION

#### FIELD OF THE INVENTION

The object of the present invention is to provide magnetic acicular particles exhibiting not only an excellent

dispersibility in vehicle due to a less amount of carbon black desorbed or fallen-off from the surfaces thereof, but also a more excellent blackness, a lower volume resistivity value and a well-controlled myristic acid-adsorption; and a magnetic recording medium exhibiting not only a smooth surface, a smaller light transmittance and a lower surface electrical resistivity value, but also a small friction coefficient and an excellent running durability.

#### PRIOR ART

With a development of miniaturized, lightweight video or audio magnetic recording and reproducing apparatuses for long-time recording, magnetic recording media such as a magnetic tape and magnetic disk have been increasingly and strongly desired to have a higher performance, namely, a higher recording density, higher output characteristic, in particular, an improved frequency characteristic and a lower noise level.

Especially, video tapes have recently been desired more and more to have a higher picture quality, and the frequencies of carrier signals recorded in recent video tapes are higher than those recorded in conventional video tapes. In other words, the signals in the short-wave region have come to be used, and as a result, the magnetization depth from the surface of a magnetic tape has come to be remarkably small.

In order to enhance output characteristics of magnetic

recording media, especially an S/N ratio thereof with respect to signals having a short wavelength, there have been demanded fineness of magnetic particles, reduction in thickness of a magnetic recording layer, high dispersibility of magnetic particles and surface smoothness of a magnetic coating film.

On the other hand, at the present time, the end position of a magnetic recording medium such as magnetic tapes has been detected by sensing a high light transmittance portion of the magnetic recording medium by means of a video deck. In the case where the particle size of magnetic particles dispersed in the magnetic recording layer become finer and the thickness of the magnetic recording medium is reduced in order to meet the requirement for high performance of the magnetic recording medium as described hereinbefore, the magnetic recording medium shows a high light transmittance as a whole, so that it has been difficult to detect the end position thereof by means of the video deck. In order to solve this problem, carbon black fine particles have been added to the magnetic recording layer in an amount of usually about 6 to 12 parts by weight based on 100 parts by weight of the magnetic particles, thereby reducing the light transmittance of the magnetic recording medium. For this reason, in current videotapes, it is essential to add carbon black fine particles, etc., to the magnetic recording layer thereof.

However, when a large amount of such non-magnetic

carbon black fine particles are added to the magnetic recording layer, the magnetic recording medium suffers from deterioration in signal recording property, thereby hindering high-density recording thereon, and the reduction in thickness of the magnetic recording layer becomes incapable. Further, due to the fact that the carbon black fine particles have a large BET specific surface area value, and are deteriorated in solvent-wettability, it has been difficult to disperse these carbon black fine particles in vehicle, thereby failing to obtain a magnetic recording medium having a smooth surface.

Further, in the case where the magnetic recording medium has a high surface electrical resistivity, the electrostatic charge amount thereof is increased, so that cut chips or dusts tend to adhere onto the surface of the magnetic recording medium upon the production or use thereof, thereby causing such a problem that the dropout frequently occurs. Therefore, in order to reduce not only the light transmittance of the magnetic recording medium but also the surface electrical resistivity thereof, especially below about  $10^8 \Omega/\text{cm}^2$ , the carbon black fine particles have been conventionally added to the magnetic recording layer of the magnetic recording medium.

However, as described above, in the case where the amount of such carbon black fine particles or the like which do not contribute to magnetic properties of the magnetic recording layer, is increased, there are caused such

problems that the magnetic recording medium suffers from deterioration in signal recording property, the reduction in thickness of the magnetic recording layer becomes incapable, and further the surface smoothness of the magnetic recording layer is deteriorated.

Also, since the carbon black fine particles are bulky particles having a bulk density as low as about  $0.1 \text{ g/cm}^3$ , the handling property and workability thereof are deteriorated. In addition, it has been pointed out that the use of such carbon black fine particles causes problems concerning safety and hygiene such as carcinogenesis.

Magnetic recording media have been continuously required to enhance performances thereof. In particular, it has been strongly required to improve physical properties of these magnetic recording media such as running property in addition to the above-described high-density recording property.

The running property of magnetic recording media can be ensured by adding a fatty acid such as myristic acid or stearic acid (hereinafter referred to merely as "myristic acid") in an amount of usually about 0.5 to 5 % by weight based on the weight of magnetic particles, into a magnetic recording layer generally formed as an upper layer of the respective magnetic recording medium, and then allowing the myristic acid to be gradually oozed out on the surface of the magnetic recording layer so as to render the surface slidable.

When the amount of the myristic acid oozed out on the surface of the magnetic recording layer is too small, it is not possible to ensure a good running property of the magnetic recording media. On the contrary, when a large amount of the myristic acid is added to the magnetic recording layer so as to allow a large amount of myristic acid to be subsequently oozed out on the surface thereof, the myristic acid is preferentially adsorbed onto the surface of each magnetic particle dispersed in the magnetic recording layer, thereby inhibiting the magnetic particles from being contacted with or adsorbed into resins. As a result, it is difficult to disperse the magnetic particles in vehicle. Also, the increase in amount of the myristic acid as a non-magnetic component causes deterioration in magnetic properties of the magnetic recording media. Further, since the myristic acid acts as a plasticizer, there arise problems such as deterioration in mechanical strength of the magnetic recording media.

Recently, with further reduction in thickness of the magnetic recording layer, the absolute amount of myristic acid added to the magnetic recording layer is decreased. In addition, since the particle size of the magnetic particles have become much finer in order to meet the requirement of high-density recording, the BET specific surface area thereof is increased, so that a large amount of myristic acid is absorbed onto the surfaces of the magnetic particles. Under these conditions, it is more and more



difficult to properly adjust the amount of the myristic acid oozed out on the surface of the magnetic recording layer by the amount of the myristic acid added into the magnetic recording layer, thereby ensuring a good running property of the magnetic recording layer.

Accordingly, in a tendency of the reduction in thickness of the magnetic recording layer, it has been strongly required to properly adjust the amount of myristic acid oozed out on the surface of the magnetic recording layer and ensure a good running property of the magnetic recording media.

In order to improve electrical resistance and running durability of the magnetic recording media, there have been proposed such magnetic particles on the surfaces of which carbon and/or graphite are deposited or adhered in an amount of 0.2 to 10.0 % by weight based on the weight of the magnetic particles (corresponding to 0.2 to 11.11 parts by weight based on 100 parts by weight of the magnetic particles) by various methods such as gas-phase growth, e.g., chemical vapor deposition (CVD) or physical vapor deposition (PVD), reduction of organic compounds, and thermal decomposition or incomplete combustion of hydrocarbons (Japanese Patent Application Laid-Open (KOKAI) No. 10-269558).

#### TECHNICAL PROBLEM TO BE SOLVED BY THE INVENTION

At present, it has been strongly demanded to provide

magnetic recording media which exhibit not only a smooth surface, a smaller light transmittance and a lower surface electrical resistivity value, but also a small friction coefficient and an excellent running durability. However, magnetic recording media satisfying all of these properties have not been obtained until now.

Since in the magnetic particles described in Japanese Patent Application Laid-Open (KOKAI) No. 10-269558, carbon black is desorbed or fallen-off from the surfaces thereof, the magnetic recording medium produced by using these magnetic particles is deteriorated in gloss, surface roughness, linear absorption, friction coefficient and running durability.

It is a technical subject of the present invention to provide magnetic acicular particles for producing a magnetic recording medium exhibiting not only a smooth surface, a smaller light transmittance and a lower surface electrical resistivity value, but also a small friction coefficient and an excellent running durability.

#### MEANS FOR SOLVING THE TECHNICAL PROBLEM

The technical subject described above is accomplished by the present invention as follows.

In an aspect of the present invention, there is provided magnetic acicular particles for a magnetic recording medium, comprising black magnetic acicular composite particles having an average particle diameter of

0.051 to 0.35  $\mu\text{m}$  and an absorption amount of myristic acid of 0.01 to 0.3  $\text{mg}/\text{m}^2$ , and comprising:

as core particles, magnetic acicular cobalt-coated iron oxide particles or magnetic acicular metal particles containing iron as a main component,

a coating formed on surface of said core particles, comprising organosilane compounds obtainable from alkoxy silane compounds, or polysiloxanes, and

a carbon black adhered on at least a part of said coating in an amount of from more than 10 to 40 parts by weight based on 100 parts by weight of the core particles.

In another aspect of the present invention, there is provided magnetic acicular particles for a magnetic recording medium, comprising black magnetic acicular composite particles having an average particle diameter of 0.051 to 0.35  $\mu\text{m}$  and an absorption amount of myristic acid of 0.01 to 0.3  $\text{mg}/\text{m}^2$ , and comprising:

magnetic acicular cobalt-coated iron oxide particles or magnetic acicular metal particles containing iron as a main component,

as a lower layer, a coat formed on the surface of said magnetic acicular cobalt-coated iron oxide particles or magnetic acicular metal particles containing iron as a main component, comprising at least one compound selected from the group consisting of hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon,

a coating formed on the lower layer, comprising

organosilane compounds obtainable from alkoxysilane compounds, or polysiloxanes, and

a carbon black adhered on at least a part of said coating in an amount of from more than 10 to 40 parts by weight based on 100 parts by weight of the core particles.

In other aspect of the present invention, there is provided a magnetic recording medium comprising:

a non-magnetic base film; and

a magnetic recording layer comprising a binder resin and as magnetic particles, magnetic acicular particles as defined in each of the above-mentioned aspects.

The constitution of the present invention will be explained in more detail.

First, the magnetic acicular particles for the magnetic recording medium according to the present invention is explained.

The magnetic acicular particles according to the present invention comprise as a core particle, black magnetic acicular composite particles comprising magnetic acicular cobalt-coated iron oxide particles or magnetic acicular metal particles containing iron as a main component, a coating layer comprising organosilane compounds obtainable from alkoxysilane compounds or polysiloxanes, which is formed on the surface of each core particle, and carbon black coat which are formed on at least a part of the coating layer comprising the organosilane compounds or the polysiloxanes.

As the magnetic acicular cobalt-coated iron oxide particles used in the core particles in the present invention, there may be exemplified magnetic acicular cobalt-coated iron oxide particles obtained by coating with cobalt, both cobalt and iron or the like the surface of acicular magnetite particles ( $\text{FeO}_x \cdot \text{Fe}_2\text{O}_3$ ;  $0 < x < 1$ ), acicular maghemite particles ( $\gamma\text{-Fe}_2\text{O}_3$ ), acicular berthollide compounds particles which are intermediate oxides between maghemite and magnetite.

As the magnetic acicular metal particles containing iron as a main component used in the core particles in the present invention, there may be exemplified magnetic acicular metal iron particles or magnetic acicular metal particles containing iron as a main component which contain elements other than Fe such as Co, Al, Ni, P, Zn, Si, B or rare earth elements.

The core particles used in the present invention have an acicular shape. Meanwhile, the "acicular" used herein means "spindle-shaped", "rice grain-like" or the like in addition to literally "acicular or needle-like".

As to the particle size of the core particles used in the present invention, the average major axial diameter thereof is preferably 0.05 to 0.34  $\mu\text{m}$ , more preferably 0.05 to 0.33  $\mu\text{m}$ , still more preferably 0.05 to 0.32  $\mu\text{m}$ .

When the average major axis diameter of the core particles is more than 0.34  $\mu\text{m}$ , the obtained black magnetic acicular composite particles also may become large

particles. In the case where such large particles are used for forming a magnetic recording layer, the surface smoothness of the magnetic recording layer tends to be deteriorated. On the other hand, when the average particle size is less than  $0.05\text{ }\mu\text{m}$ , the intermolecular force between the particles may be increased due to the reduction in particle size, so that agglomeration of the particles tends to be caused. Therefore, it becomes difficult to uniformly coat the surfaces of the core particle with the alkoxysilane compounds or polysiloxanes, and to uniformly form the carbon black coat on the surface of the coating layer comprising the alkoxysilane compounds or polysiloxanes.

The aspect ratio of the core particles used in the present invention is preferably 2.0:1 to 20.0:1, more preferably 2.5:1 to 18.0:1, still more preferably 3.0:1 to 15.0:1.

When the aspect ratio is more than 20.0:1, the core particles may tend to be entangled with each other, and it also may become difficult to uniformly coat the surfaces of the core with the alkoxysilane compounds and to uniformly form the carbon black coat on the surface of the coating layer comprising the alkoxysilane compounds. On the other hand, when the aspect ratio is less than 2.0:1, the strength of the coating film of the magnetic recording medium may be low.

The geometrical standard deviation value of the major axis diameter of the core particles used in the present

invention is usually not more than 2.0, preferably not more than 1.8, more preferably not more than 1.6. When the geometrical standard deviation value thereof is more than 2.0, coarse particles may be contained therein, so that the core particles may be inhibited from being uniformly dispersed. Therefore, it may also become difficult to uniformly coat the surfaces of the core particles with the alkoxy silane compounds and to uniformly form the carbon black coat on the surface of the coating layer comprising the alkoxy silane compounds. The lower limit of the geometrical standard deviation value is 1.01. It is industrially difficult to obtain particles having a geometrical standard deviation value of less than 1.01.

The BET specific surface area of the core particles used in the present invention is preferably 20 to 150 m<sup>2</sup>/g, more preferably 25 to 120 m<sup>2</sup>/g, still more preferably 28 to 100 m<sup>2</sup>/g. When the BET specific surface area is less than 20 m<sup>2</sup>/g, the core particles may become coarse, or the sintering between the particles may be caused, so that the obtained black magnetic acicular composite particles also may become coarse particles and tend to be deteriorated in smooth surface of the magnetic recording layer. When the BET specific surface area value is more than 150 m<sup>2</sup>/g, the particles may tend to be agglomerated together due to the increase in intermolecular force between the particles because of the fineness thereof, so that it may become difficult to uniformly coat the surfaces of the core

particles with the alkoxysilane compounds and to uniformly form the carbon black coat on the surface of the coating layer comprising the alkoxysilane compounds.

The blackness of the core particles used in the present invention, is usually more than 18.0 when represented by  $L^*$  value, and the upper limit thereof is usually 34.0, preferably 32.0 when represented by  $L^*$  value. When the  $L^*$  value exceeds 34.0, the lightness of the particles may be high, so that it may be difficult to obtain black magnetic acicular composite particles having a sufficient blackness.

The volume resistivity value of the core particles is usually not less than  $5 \times 10^{10}$   $\Omega \cdot \text{cm}$ .

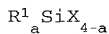
The myristic acid-adsorption of the core particles is usually 0.4 to 1.5 mg/m<sup>2</sup>.

As to the magnetic properties of the core particles used in the present invention, in case of magnetic acicular cobalt-coated iron oxide particles, the coercive force value thereof is preferably 500 to 1700 Oe, more preferably 550 to 1700 Oe; the saturation magnetization value is preferably 60 to 90 emu/g, more preferably 65 to 90 emu/g. In case of magnetic acicular metal particles containing iron as a main component, the coercive force value thereof is preferably 800 to 3500 Oe, more preferably 900 to 3500 Oe; the saturation magnetization value is preferably 90 to 170 emu/g, more preferably 100 to 170 emu/g.

The organosilane compounds obtainable from



alkoxysilane compounds (hereinafter referred to merely as "organosilane compounds"), may be produced by drying or heat-treating alkoxysilane compounds represented by the formula:



wherein

$R^1$  is  $C_6H_5-$ ,  $(CH_3)_2CHCH_2-$  or  $n-C_{2m+1}H_{4m+3}-$

X is  $CH_3O-$  or  $C_2H_5O-$ ;

m: an integer of 1 to 18

a: an integer of 0 to 3

Specific examples of the alkoxysilane compounds may include methyltriethoxysilane, dimethyldiethoxysilane, phenyltriethoxysilane, diphenyldiethoxysilane, methyltrimethoxysilane, dimethyldimethoxysilane, phenyltrimethoxysilane, diphenyldimethoxysilane, isobutyltrimethoxysilane, decyltrimethoxysilane or the like.

Among these alkoxysilane compounds, in view of the desorption percentage and the adhering effect of carbon black, methyltriethoxysilane, methyltrimethoxysilane, dimethyldimethoxysilane, isobutyltrimethoxysilane and phenyltriethoxysilane are preferred, and methyltriethoxysilane and methyltrimethoxysilane are more preferred.

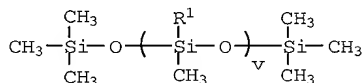
The coating amount of the organosilane compounds is preferably 0.02 to 5.0 % by weight, more preferably 0.03 to 4.0 % by weight, still more preferably 0.05 to 3.0 % by

weight (calculated as Si) based on the weight of the core particles coated with the organosilane compounds.

When the coating amount of the organosilane compounds is less than 0.02 % by weight, it becomes difficult to coat the carbon black on the surfaces of the core particles in such an amount enough to improve the blackness, volume resistivity and absorption amount of myristic acid thereof.

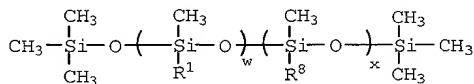
On the other hand, when the coating amount of the organosilane compounds is more than 5.0 % by weight, it is possible to adhere fully carbon black, but the adhering effect is already saturated and, therefore, the use of such a large coating amount of the organosilane compounds is unnecessary and meaningless.

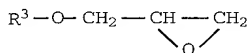
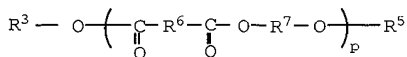
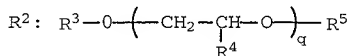
As the polysiloxanes used in the present invention, there may be exemplified polysiloxanes, modified polysiloxanes and terminal-modified polysiloxanes represented by the formulae:



R<sup>1</sup>: H, CH<sub>3</sub>,

v: 15 to 450





$R^3$ ,  $R^6$  and  $R^7$ :  $-(CH_2)_1-$  and may be the same or different,

$R^4$  and  $R^8$ :  $-(CH_2)_m-CH_3$ ,

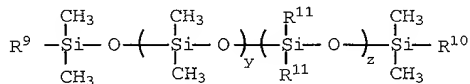
$R^5$ :  $-OH$ ,  $-COOH$ ,  $-CH=CH_2$ ,  $-C=CH_3$  or  $-(CH_2)_n-CH_3$ ,

$l$ : 1 to 15,

$m$ ,  $n$ : 0 to 15,

$w$ : 1 to 50

$x$ : 1 to 300



$R^9$  and  $R^{10}$ :  $-OH$ ,  $R^{12}OH$  or  $R^{13}COOH$  and may be the same or different,

$R^{11}$ :  $-CH_3$  or  $-C_6H_5$ ,

$R^{12}$  and  $R^{13}$ :  $-(CH_2)_p-$ ,

$l$ : 1 to 15,

$y$ : 1 to 200,

$z$ : 0 to 100

In view of the desorption percentage and the adhering effect of carbon black, polysiloxanes having methyl hydrogen siloxane units, the polysiloxanes modified with the polyethers and the polysiloxanes whose terminals are modified with carboxylic acid groups are preferred.

The coating amount of the polysiloxanes is preferably 0.02 to 5.0 % by weight, more preferably 0.03 to 4.0 % by weight, still more preferably 0.05 to 3.0 % by weight (calculated as Si) based on the weight of the core particles coated with the polysiloxanes.

When the coating amount of the polysiloxanes is less than 0.02 % by weight, it becomes difficult to coat the carbon black on the surfaces of the core particles in such an amount enough to improve the blackness, volume resistivity and absorption amount of myristic acid thereof.

On the other hand, when the coating amount of the polysiloxanes is more than 5.0 % by weight, it is possible to adhere fully carbon black, but the adhering effect is already saturated and, therefore, the use of such a large coating amount of the polysiloxanes is unnecessary and meaningless.

The carbon black composed of at least two layers of carbon black in which the interlaminar thereof is adhered, is formed on the coating layer composed of the organosilane compounds obtainable from the alkoxysilane compounds or the polysiloxanes.

As the carbon black fine particles used in the present invention, there may be exemplified commercially available carbon blacks such as furnace black, channel black or the like. Specific examples of the commercially available carbon blacks usable in the present invention, may include #3050, #3150, #3250, #3750, #3950, MA100, MA7, #1000, #2400B, #30, MA77, MA8, #650, MA11, #50, #52, #45, #2200B, MA600, etc. (tradename, produced by MITSUBISHI CHEMICAL CORP.), SEAST 9H, SEAST 7H, SEAST 6, SEAST 3H, SEAST 300, SEAST FM, etc. (tradename, produced by TOKAI CARBON CO., LTD.), Raven 1250, Raven 860, Raven 1000, Raven 1190 ULTRA, etc. (tradename, produced by COLOMBIAN CHEMICALS COMPANY), Ketchen black EC, Ketchen black EC600JD, etc. (tradename, produced by KETCHEN INTERNATIONAL CO., LTD.), BLACK PEARLS-L, BLACK PEARLS 1000, BLACK PEARLS 4630, VULCAN XC72, REGAL 660, REGAL 400, etc. (tradename, produced by CABOTT SPECIALTY CHEMICALS INK CO., LTD.), or the like.

In the consideration of the reducing effect of the myristic acid-adsorption, the carbon black fine particles having a pH value of not more than 9.0 is preferred. Especially, there may be exemplified #3050, #3150, #3250, #3750, #3950, MA100, MA7, #1000, #2400B, #30, MA77, MA8, #650, MA11, #50, #52, #45, #2200B, MA600 (tradename, produced by MITSUBISHI CHEMICAL CORP.), SEAST 9H, SEAST 7H, SEAST 6, SEAST 3H, SEAST 300, SEAST FM (tradename, produced by TOKAI CARBON CO., LTD.), Raven 1250, Raven 860, Raven 1000, Raven 1190 ULTRA (tradename, produced by COLOMBIAN

CHEMICALS COMPANY), BLACK PEARLS-L, BLACK PEARLS 1000, BLACK PEARLS 4630, REGAL 660, REGAL 400 (tradename, produced by CABOT SPECIALTY CHEMICALS INK CO., LTD.).

Further, in the consideration of more uniform coat of carbon black to the coating layer comprising at least one organosilicon compound, the carbon black fine particles having a DBP oil absorption of not more than 180 ml/100 g is preferred. Especially, there may be exemplified #3050, #3150, #3250, MA100, MA7, #1000, #2400B, #30, MA77, MA8, #650, MA11, #50, #52, #45, #2200B, MA600 (tradename, produced by MITSUBISHI CHEMICAL CORP.), SEAST 9H, SEAST 7H, SEAST 6, SEAST 3H, SEAST 300, SEAST FM (tradename, produced by TOKAI CARBON CO., LTD.), Raven 1250, Raven 860, Raven 1000, Raven 1190 ULTRA (tradename, produced by COLOMBIAN CHEMICALS COMPANY), BLACK PEARLS-L, BLACK PEARLS 1000, BLACK PEARLS 4630, REGAL 660, REGAL 400 (tradename, produced by CABOT SPECIALTY CHEMICALS INK CO., LTD.).

The average particle size of the carbon black fine particles used is preferably 0.002 to 0.05  $\mu\text{m}$ , more preferably 0.005 to 0.035  $\mu\text{m}$ .

When the average particle size of the carbon black fine particles used is less than 0.002  $\mu\text{m}$ , the carbon black fine particles used are too fine to be well handled.

On the other hand, when the average particle size of the carbon black fine particles used is more than 0.05  $\mu\text{m}$ , since the carbon black fine particles used is much larger, it is necessary to apply a larger mechanical shear force for

forming the uniform carbon black coat on the coating layer composed of the alkoxysilane compounds or the polysiloxanes, thereby rendering the coating process industrially disadvantageous.

The amount of the carbon black coat (hereinafter referred to merely as "first carbon black coat") formed on the coating layer composed of the organosilane compounds obtainable from the alkoxysilane compounds or the polysiloxanes, is usually 1 to 10 parts by weight, preferably 3 to 10 parts by weight based on 100 parts by weight of the core particles.

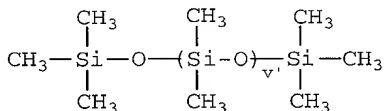
When the amount of the carbon black is less than 1 part by weight, the blackness of the resultant black magnetic acicular composite particles may be unsatisfactory because of insufficient amount of the carbon black coat formed onto the coating layer. As a result, in case of adding carbon black constituting a second carbon black coat so that the total amount of carbon black exceeds 10 parts by weight based on 100 parts by weight of the core particles, the percentage of desorption of carbon black become to increase and as a result, it becomes difficult to improve the blackness, volume resistivity and absorption amount of myristic acid thereof.

When the amount of the carbon black is more than 10 parts by weight, the carbon black may tend to be desorbed from the surface of the core particle and as a result, the obtained black magnetic acicular composite hematite

particles can show that the carbon black may tend to be desorbed therefrom.

The amount of a layer composed of carbon black (hereinafter referred to merely as "second carbon black coat") which is formed onto the surface of the first carbon black coat is usually 1 to 30 parts by weight based on 100 parts by weight of the core particles. When the amount of the carbon black is more than 30 parts by weight, the percentage of desorption of carbon black become to increase.

In the present invention, the first and second carbon black coats may be integrated together by bonding carbon black of the respective coats with each other using an adhesive. In order to firmly and uniformly bond the carbon black coats with each other and control the myristic acid-adsorption to an appropriate level, it is preferred to use as the adhesive, dimethyl polysiloxane represented by the following formula:



wherein  $v'$  is an integer of 15 to 450.

The amount of the adhesive used is 0.1 to 5 parts by weight based on 100 parts by weight of the core particles.

When the amount of the adhesive used is less than 0.1 part by weight, it may be difficult to sufficiently bond the second carbon black coat onto the first carbon black coat.



As a result, it may be difficult to improve the myristic acid-adsorption of the obtained black magnetic acicular composite particles.

When the amount of the adhesive used is more than 5 parts by weight, although the carbon black coats can be sufficiently bonded together, the effect is already saturated and, therefore, the use of such a large amount of the adhesive is unnecessary and meaningless.

The total amount of carbon black is in the range of from more than 10 to 40 parts by weight based on 100 parts by weight of the core particles.

When the total amount of carbon black is not less than 10 parts by weight, it is difficult to lower a myristic acid absorption to  $0.3 \text{ mg/m}^2$ . When the total amount of carbon black is more than 40 parts by weight, the myristic acid absorption become not more than  $0.01 \text{ mg/m}^2$ , and as a result, it is difficult to control the amount of myristic acid oozed onto the surface of the magnetic recording layer.

In the consideration of the myristic acid-adsorption and carbon black desorption percentage, the total amount of carbon black coat is preferably 11 to 38 parts by weight, more preferably 12 to 35 parts by weight based on 100 parts by weight of the core particles.

The thickness of carbon black coat is preferably not more than  $0.03 \text{ }\mu\text{m}$ , more preferably not more than  $0.02 \text{ }\mu\text{m}$ , still more preferably not more than  $0.01 \text{ }\mu\text{m}$ .

The particle shape and size of the magnetic acicular

particles according to the present invention, are considerably varied depending upon those of the core particles. More specifically, the particle shape or configuration of the magnetic acicular particles is similar to that of the core particles, and the particle size of the magnetic acicular particles is slightly larger than that of the core particles.

That is, the magnetic acicular particles according to the present invention, have an average major axial diameter of usually 0.051 to 0.35  $\mu\text{m}$ , preferably 0.051 to 0.34  $\mu\text{m}$ , more preferably 0.051 to 0.33  $\mu\text{m}$ ; and an aspect ratio of usually 2.0:1 to 20.0:1, preferably 2.5:1 to 18.0:1, more preferably 3.0:1 to 15.0:1.

When the average major axial diameter is more than 0.35  $\mu\text{m}$ , the magnetic acicular particles become too large. In the case where such large particles are used, the obtained magnetic recording layer may tend to be deteriorated in surface smoothness of coating film. When the average major axial diameter is less than 0.051  $\mu\text{m}$ , the intermolecular force between the particles may become too large due to fineness thereof, so that the magnetic acicular particles may tend to be agglomerated together, resulting in deteriorated dispersibility in vehicle upon the production of a magnetic coating composition.

When the aspect ratio is more than 20.0:1, the particles may tend to be entangled or interlaced with each other, sometimes resulting in deteriorated dispersibility in

vehicle upon the production of a magnetic coating composition and increased viscosity of the magnetic coating composition. When the aspect ratio is less than 2.0:1, the strength of coating film of the obtained magnetic recording medium using such particles may become small.

The geometrical standard deviation value of major axial diameters of the magnetic acicular particles according to the present invention is usually not more than 2.0. When the geometrical standard deviation value is more than 2.0, coarse particles may be present in the magnetic acicular particles, thereby adversely affecting the surface smoothness of the obtained coating film. In the consideration of the surface smoothness of coating film, the geometrical standard deviation value is preferably not more than 1.8, more preferably not more than 1.6. In the consideration of industrial productivity, the geometrical standard deviation value is not less than 1.01. Meanwhile, the particles having a geometrical standard deviation value of less than 1.01 are difficult to industrially produce.

The magnetic acicular particles according to the present invention have a BET specific surface area of preferably 21 to 160 m<sup>2</sup>/g, more preferably 26 to 130 m<sup>2</sup>/g, still more preferably 29 to 110 m<sup>2</sup>/g. When the BET specific surface area is less than 21 m<sup>2</sup>/g, the magnetic acicular particles may tend to become coarse or be sintered together. In the case where such particles are used to produce a magnetic recording layer, the obtained coating film may tend

to be deteriorated in surface smoothness. When the BET specific surface area is more than  $160 \text{ m}^2/\text{g}$ , the intermolecular force between the particles may be increased due to fineness thereof. As a result, the obtained particles may tend to be agglomerated together, resulting in deteriorated dispersibility in vehicle upon the production of magnetic coating composition.

As to the blackness of the magnetic acicular particles, the upper limit of the  $L^*$  value thereof is usually 22, preferably not more than 21, more preferably not more than 20. When the  $L^*$  value is more than 22, the lightness of the particles becomes too high, thereby failing to obtain particles having a sufficient blackness. The lower limit of the  $L^*$  value thereof is 15.

The magnetic acicular particles have a volume resistivity value of preferably not more than  $1.0 \times 10^6$   $\cdot\cdot\text{cm}$ , more preferably  $1.0 \times 10^3$  to  $5.0 \times 10^5$   $\cdot\cdot\text{cm}$ , still more preferably  $1.0 \times 10^3$  to  $1.0 \times 10^5$   $\cdot\cdot\text{cm}$ . When the volume resistivity value is more than  $1.0 \times 10^6$   $\cdot\cdot\text{cm}$ , it is difficult to sufficiently reduce the surface electrical resistivity value of the obtained magnetic recording medium.

The magnetic acicular particles of the present invention, have a myristic acid absorption of usually 0.01 to  $0.3 \text{ mg}/\text{m}^2$ , preferably 0.01 to  $0.29 \text{ mg}/\text{m}^2$ , more preferably 0.01 to  $0.28 \text{ mg}/\text{m}^2$ .

When the myristic acid-adsorption is less than  $0.01 \text{ mg}/\text{m}^2$ , the amount of myristic acid absorbed thereinto is

small, so that it is difficult to control the amount of myristic acid oozed onto the surface of the magnetic recording layer to an appropriate level. As a result, upon the repeated use of magnetic tape, it is difficult to maintain a sufficiently low friction coefficient of the magnetic tape for a long period of time.

When the myristic acid-adsorption is more than 0.3 mg/m<sup>2</sup>, the amount of myristic acid absorbed therein is large, so that the amount of myristic acid oozed onto the surface of the magnetic recording layer becomes small. As a result, it is difficult to ensure the running property of the magnetic recording medium.

The carbon black desorption percentage of the magnetic acicular particles is preferably not more than 20%, more preferably not more than 10%. When the carbon black desorption percentage is more than 20%, the obtained particles may tend to be inhibited from uniformly dispersed in vehicle due to desorbed and liberated carbon black upon the production of magnetic recording media.

As to magnetic properties of the black magnetic acicular composite particles according to the present invention, in the case where the magnetic acicular cobalt-coated iron oxide particles are used as the core particles, the coercive force value thereof is preferably 500 to 1,700 Oe, more preferably 550 to 1,700 Oe; and the saturation magnetization value thereof is preferably 60 to 90 emu/g, more preferably 65 to 90 emu/g. In the case where the

magnetic acicular metal particles containing iron as a main component are used as the core particles, the coercive force value thereof is preferably 800 to 3,500 Oe more preferably 900 to 3,500 Oe; and the saturation magnetization value thereof is preferably 90 to 170 emu/g, more preferably 100 to 170 emu/g.

The surface of the core particle may be coated with at least one selected from the group consisting of a hydroxide of aluminum, an oxide of aluminum, a hydroxide of silicon and an oxide of silicon (hereinafter referred to as "hydroxides of aluminum or the like"). When the magnetic acicular particles obtained by using as core particles the magnetic acicular particles which are coated with the hydroxides of aluminum or the like, are dispersed in a vehicle, since it is possible to more effectively reduce the carbon black desorption percentage, it is more easy to improve the dispersibility thereof.

The amount of the hydroxides of aluminum or the like coat is preferably 0.01 to 20 % by weight (calculated as Al and/or  $\text{SiO}_2$ ) based on the total weight of the core particles coated.

If it is less than 0.01 % by weight (calculated as Al and/or  $\text{SiO}_2$ ) based on the total weight of the core particles coated, since there can not be obtained an effect of reducing the percentage of carbon black desorbed or fallen-off from the surfaces of the core particles, the dispersibility-improving effect by coating therewith may be

insufficient.

When the coating amount of the hydroxide of aluminum or the like is more than 20% by weight, although there can be obtained a sufficient effect of reducing the percentage of carbon black desorbed or fallen-off from the surfaces of the core particles, the effect is already saturated and, therefore, the use of such a large coating amount of the hydroxide of aluminum or the like is unnecessary and meaningless.

The particle size, geometrical standard deviation value, BET specific surface area, blackness L\* value, volume resistivity, magnetic properties and myristic acid-adsorption of the magnetic acicular particles wherein the surface of the core particle is coated with the hydroxides of aluminum or the like according to the present invention, are substantially the same as those of the magnetic acicular particles wherein the core particle is uncoated with the hydroxides of aluminum or the like according to the present invention.

In addition, the desorption percentage of carbon black of the magnetic acicular particles wherein the surface of the core particle is coated with the hydroxides of aluminum or the like is more improved as compared with that of the magnetic acicular particles wherein the core particle is uncoated therewith. The carbon black desorption percentage of the magnetic acicular particles wherein the surface of the core particle is coated with the hydroxides of aluminum

or the like, is preferably not more than 10 %, more preferably not more than 5 %.

Next, the magnetic recording medium of the present invention is described.

The magnetic recording medium according to the present invention comprises:

a non-magnetic base film; and

a magnetic recording layer formed on the non-magnetic base film, comprising a binder resin and the black magnetic acicular composite particles.

As the non-magnetic base film, the following materials which are at present generally used for the production of a magnetic recording medium are usable as a raw material: a synthetic resin such as polyethylene terephthalate, polyethylene, polypropylene, polycarbonate, polyethylene naphthalate, polyamide, polyamideimide and polyimide; foil and plate of a metal such as aluminum and stainless steel; and various kinds of paper. The thickness of the non-magnetic base film varies depending upon the material, but it is usually about 1.0 to 300  $\mu\text{m}$ , preferably 2.0 to 200  $\mu\text{m}$ .

In the case of a magnetic disc, polyethylene terephthalate is usually used as the non-magnetic base film, and the thickness thereof is usually 50 to 300  $\mu\text{m}$ , preferably 60 to 200  $\mu\text{m}$ . In a magnetic tape, when polyethylene terephthalate is used as the non-magnetic base film, the thickness thereof is usually 3 to 100  $\mu\text{m}$ , preferably 4 to 20  $\mu\text{m}$ ; when polyethylene naphthalate is



used, the thickness thereof is usually 3 to 50  $\mu\text{m}$ , preferably 4 to 20  $\mu\text{m}$ ; and when polyamide is used, the thickness thereof is usually 2 to 10  $\mu\text{m}$ , preferably 3 to 7  $\mu\text{m}$ .

As the binder resin used in the present invention, the following resins which are at present generally used for the production of a magnetic recording medium are usable: vinyl chloride-vinyl acetate copolymer, polyurethane resin, vinyl chloride-vinyl acetate-maleic acid copolymer, urethane elastomer, butadiene-acrylonitrile copolymer, polyvinyl butyral, cellulose derivative such as nitrocellulose, polyester resin, synthetic rubber resin such as polybutadiene, epoxy resin, polyamide resin, polyisocyanate, electron radiation curing acryl urethane resin and mixtures thereof.

Each of these resin binders may contain a functional group such as  $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{SO}_3\text{M}$ ,  $-\text{OPO}_2\text{M}_2$  and  $-\text{NH}_2$ , wherein M represents H, Na or K. With the consideration of the dispersibility of the black magnetic acicular composite particles, a binder resin containing a functional group  $-\text{COOH}$  or  $-\text{SO}_3\text{M}$  is preferable.

The thickness of the magnetic recording layer obtained by applying the magnetic coating composition on the surface of the non-magnetic base film and dried, is usually in the range of 0.01 to 5.0  $\mu\text{m}$ . If the thickness is less than 0.01  $\mu\text{m}$ , uniform coating may be difficult, so that unfavorable phenomenon such as unevenness on the coating surface is

observed. On the other hand, when the thickness exceeds 5.0  $\mu\text{m}$ , it may be difficult to obtain desired signal recording property due to an influence of diamagnetism. The preferable thickness is in the range of 0.1 to 4.0  $\mu\text{m}$ .

The mixing ratio of the magnetic acicular particles with the binder resin is usually 5 to 2000 parts by weight, preferably 100 to 1000 parts by weight based on 100 parts by weight of the binder resin.

When the amount of the magnetic acicular particles blended is less than 5 parts by weight, the obtained magnetic coating composition contains a too small amount of the magnetic acicular particles. As a result, when a coating film is produced from such a magnetic coating composition, it is not possible to obtain a coating film in which the magnetic acicular particles are continuously dispersed, so that the surface smoothness and the strength of the coating film become unsatisfactory. On the other hand, when the amount of the magnetic acicular particles blended is more than 2,000 parts by weight, the amount of the magnetic acicular particles becomes too large relative to that of the binder resin, so that it is not possible to sufficiently disperse the magnetic acicular particles in the magnetic coating composition. As a result, when a coating film is produced from such a magnetic coating composition, it is difficult to obtain a coating film having a sufficiently smooth surface. Further, since the magnetic acicular particles cannot be sufficiently bound with each other by

the binder resin, the obtained coating film tends to become brittle.

In the magnetic recording medium according to the present invention, the amount of carbon black added to the magnetic recording layer thereof can be reduced to usually less than 6 parts by weight, preferably less than 5 parts by weight, more preferably less than 3 parts by weight based on 100 parts by weight of the magnetic acicular particles.

Further, in the case where the black magnetic acicular composite particles having a large particle size, are used as magnetic particles, it can be expected to omit the addition of the carbon black to the magnetic recording layer.

Incidentally, the magnetic recording layer may optionally contain a lubricant, an abrasive, an anti-static agent or the like which are usually used for the production of magnetic recording media, in an amount of 0.1 to 50 parts by weight based on 100 parts of the binder resin.

In case of using the magnetic acicular particles, wherein the magnetic acicular cobalt-coated iron oxide particles are used as core particles, which are coated with no hydroxides of aluminum or the like, the magnetic recording medium of the present invention has a coercive force of usually 500 to 1,700 Oe, preferably 550 to 1,700 Oe; a squareness (residual magnetic flux density  $B_r$ /saturation magnetic flux density  $B_m$ ) of usually 0.85 to 0.95, preferably 0.86 to 0.95; a gloss (of the coating film)

of usually 165 to 300 %, preferably 170 to 300 %; a surface roughness Ra (of the coating film) of usually not more than 11.5 nm, preferably 2.0 to 10.5 nm, more preferably 2.0 to 9.5 nm, a Young's modulus of usually 124 to 160, preferably 125 to 160; a linear adsorption coefficient (of the coating film) of usually 1.75 to 10.0  $\mu\text{m}^{-1}$ , preferably 1.80 to 10.0  $\mu\text{m}^{-1}$ ; and a surface electrical resistivity of usually not more than  $1.0 \times 10^8 \Omega/\text{cm}^2$ , preferably not more than  $7.5 \times 10^7 \Omega/\text{cm}^2$ , more preferably not more than  $5.0 \times 10^7 \Omega/\text{cm}^2$ ; a running durability time thereof of usually not less than 24 minutes, preferably not less than 25 minutes; a friction coefficient of usually 0.25 to 0.30, preferably 0.25 to 0.29.

In case of using the magnetic acicular particles, wherein the magnetic acicular metal particles containing iron as a main component are used as core particles which are coated with no hydroxides of aluminum or the like, the magnetic recording medium of the present invention has a coercive force of usually 800 to 3,500 Oe preferably 900 to 3,500 Oe; a squareness (residual magnetic flux density Br/saturation magnetic flux density Bm) of usually 0.85 to 0.95, preferably 0.86 to 0.95; a gloss (of the coating film) of usually 185 to 300 %, preferably 195 to 300 %; a surface roughness Ra (of the coating film) of usually not more than 11.5 nm, preferably 2.0 to 10.5 nm, more preferably 2.0 to 9.5 nm, a Young's modulus of usually 124 to 160, preferably 125 to 160; a linear adsorption coefficient (of the coating

film) of usually  $1.85$  to  $10.0 \mu\text{m}^{-1}$ , preferably  $1.90$  to  $10.0 \mu\text{m}^{-1}$ ; and a surface electrical resistivity of usually not more than  $1.0 \times 10^8 \Omega/\text{cm}^2$ , preferably not more than  $7.5 \times 10^7 \Omega/\text{cm}^2$ , more preferably not more than  $5.0 \times 10^7 \Omega/\text{cm}^2$ ; a running durability time thereof of usually not less than 24 minutes, preferably not less than 25 minutes; a friction coefficient of usually  $0.25$  to  $0.30$ , preferably  $0.25$  to  $0.29$ .

In case of using the magnetic acicular particles, wherein the magnetic acicular cobalt-coated iron oxide particles as core particles which are coated with hydroxides of aluminum or the like, the magnetic recording medium of the second aspect in the present invention has a coercive force of usually  $500$  to  $1,700$  Oe, preferably  $550$  to  $1,700$  Oe; a squareness (residual magnetic flux density  $B_r$ /saturation magnetic flux density  $B_m$ ) of usually  $0.85$  to  $0.95$ , preferably  $0.86$  to  $0.95$ ; a gloss (of the coating film) of usually  $170$  to  $300 \%$ , preferably  $175$  to  $300 \%$ ; a surface roughness  $R_a$  (of the coating film) of usually not more than  $10.5 \text{ nm}$ , preferably  $2.0$  to  $9.5 \text{ nm}$ , more preferably  $2.0$  to  $8.5 \text{ nm}$ , a Young's modulus of usually  $126$  to  $160$ , preferably  $127$  to  $160$ ; a linear adsorption coefficient (of the coating film) of usually  $1.75$  to  $10.0 \mu\text{m}^{-1}$ , preferably  $1.80$  to  $10.0 \mu\text{m}^{-1}$ ; and a surface electrical resistivity of usually not more than  $1.0 \times 10^8 \Omega/\text{cm}^2$ , preferably not more than  $7.5 \times 10^7 \Omega/\text{cm}^2$ , more preferably not more than  $5.0 \times 10^7 \Omega/\text{cm}^2$ ; a

running durability time thereof of usually not less than 26 minutes, preferably not less than 27 minutes; a friction coefficient of usually 0.21 to 0.26, preferably 0.21 to 0.25.

In case of using the black magnetic acicular particles, wherein the magnetic acicular metal particles containing iron as a main component as core particles which are coated with hydroxides of aluminum or the like, the magnetic recording medium the second aspect in the present invention has a coercive force of usually 800 to 3500 Oe, preferably 900 to 3500 Oe; a squareness (residual magnetic flux density  $B_r$ /saturation magnetic flux density  $B_m$ ) of usually 0.85 to 0.95, preferably 0.86 to 0.95; a gloss (of the coating film) of usually 190 to 300 %, preferably 200 to 300 %; a surface roughness  $R_a$  (of the coating film) of usually not more than 10.5 nm, preferably 2.0 to 9.5 nm, more preferably 2.0 to 8.5 nm, a Young's modulus of usually 126 to 160, preferably 127 to 160; a linear adsorption coefficient (of the coating film) of usually 1.85 to 10.0  $\mu\text{m}^{-1}$ , preferably 1.90 to 10.0  $\mu\text{m}^{-1}$ ; and a surface electrical resistivity of usually not more than  $1.0 \times 10^8 \Omega/\text{cm}^2$ , preferably not more than  $7.5 \times 10^7 \Omega/\text{cm}^2$ , more preferably not more than  $5.0 \times 10^7 \Omega/\text{cm}^2$ ; a running durability time thereof of usually not less than 26 minutes, preferably not less than 27 minutes; a friction coefficient of usually 0.21 to 0.26, preferably 0.21 to 0.25.

The magnetic acicular particles according to the

present invention can be produced by the following method.

As the core particles used in the present invention, known Co-coated magnetic acicular iron oxide particles or magnetic acicular metal particles containing iron as a main component may be used.

The coating of the core particles with the alkoxysilane compounds or the polysiloxanes may be conducted by mechanically mixing and stirring the core particles together with the alkoxysilane compounds or the polysiloxanes; or by mechanically mixing and stirring both the components together while spraying the alkoxysilane compounds or the polysiloxanes onto the core particles. In these cases, substantially whole amount of the alkoxysilane compounds or the polysiloxanes added can be applied onto the surfaces of the core particles.

In order to uniformly coat the surfaces of the core particles with the alkoxysilane compounds or the polysiloxanes, it is preferred that the core particles are preliminarily diagggregated by using a pulverizer.

As apparatus for mixing and stirring treatment of the core particles with the alkoxysilane compounds or the polysiloxanes to form the coating layer thereof, and as apparatus for mixing and stirring treatment of carbon black fine particles with the particles whose surfaces are coated with the alkoxysilane compounds or the polysiloxanes to form the carbon black coat, there may be preferably used those apparatus capable of applying a shear force to the

particles, more preferably those apparatuses capable of conducting the application of shear force, spatulate force and compressed force at the same time. As such apparatuses, there may be exemplified wheel-type kneaders, ball-type kneaders, blade-type kneaders, roll-type kneaders or the like.

Specific examples thereof may include a mix muller, a Simpson mill, a sand mill, a multi-mull, a Stotz mill, a wet pan mill, a Conner mill, Henschel mixer, a ring muller, a revolving mill, a vibrating mill, a pressure kneader, an extruder, a screw mixer or the like. Among them, a mix muller, a Simpson mill, a sand mill, a multi-mull, a Stotz mill, a wet pan mill, a Conner mill and Henschel mixer are more preferred. Especially, a mix muller, a Simpson mill, a sand mill and a multi-mull are more preferred.

In order to coat the surfaces of the core particles with the alkoxysilane compounds or the polysiloxanes as uniformly as possible, the conditions of the above mixing or stirring treatment may be appropriately controlled such that the linear load is usually 2 to 200 Kg/cm, preferably 10 to 150 Kg/cm, more preferably 15 to 100 Kg/cm; and the treating time is usually 5 to 120 minutes, preferably 10 to 90 minutes. It is preferred to appropriately adjust the stirring speed in the range of usually 2 to 2,000 rpm, preferably 5 to 1,000 rpm, more preferably 10 to 800 rpm.

The amount of the alkoxysilane compounds or the polysiloxanes added, is preferably 0.15 to 45 parts by



weight based on 100 parts by weight of the core particles. When the amount of the alkoxyasilane compounds or the polysiloxanes added, is less than 0.15 parts by weight, it becomes difficult to adhere the carbon black of 1 to 10 parts by weight for forming the first coating layer on the surfaces of the core particles. When the amount of the alkoxyasilane compounds or the polysiloxanes added, is more than 45 parts by weight, it is possible to adhere a large amount of carbon black, but the use of such a large amount thereof is unnecessary and meaningless.

After coating the surface of the core particle with the alkoxyasilane compounds or the polysiloxanes, the carbon black fine particles are added to the core particles coated with the alkoxyasilane compounds or the polysiloxanes, and the resultant mixture is mixed and stirred to form the first carbon black coat on the surfaces of the coating layer composed of the alkoxyasilane compounds or the polysiloxanes.

It is preferred that the carbon black fine particles are added little by little and slowly, especially about 5 to 60 minutes.

In order to form carbon black coat onto the coating layer composed of the alkoxyasilane compounds or the polysiloxanes as uniformly as possible, the conditions of the above mixing or stirring treatment can be appropriately controlled such that the linear load is usually 2 to 200 Kg/cm, preferably 10 to 150 Kg/cm, more preferably 15 to 100 Kg/cm; and the treating time is usually 5 to 120 minutes,

preferably 10 to 90 minutes. It is preferred to appropriately adjust the stirring speed in the range of usually 2 to 2,000 rpm, preferably 5 to 1,000 rpm, more preferably 10 to 800 rpm.

The amount of carbon black fine particles added for forming the first carbon black coat is 1 to 10 parts by weight based on 100 parts by weight of the core particles. When the amount of carbon black fine particles added is less than 1 part by weight, the amount of carbon black coat may become too small and the amount of the adhesive may become too small. As a result, it may be difficult to adhere carbon black fine particles even if the enough amount of carbon black fine particles is added for forming the second carbon black coat.

Next, the adhesive is added to the intermediate composite particles on which the first carbon black coat is formed, and the mixture is mixed and stirred together to adhere the adhesive onto the particles. Then, carbon black fine particles are further added to the obtained intermediate composite particles, and these particles are mixed and stirred together to form the carbon black coat onto the first carbon black coat, and the obtained particles may be dried or heat-treated, thereby forming the second carbon black coat on the first carbon black coat.

The mixing and stirring conditions with the adhesives may be adequately controlled such that the linear load is usually 2 to 200 Kg/cm, preferably 10 to 150 Kg/cm, more

preferably 15 to 100 Kg/cm; the treating time is usually 5 to 120 minutes, preferably 10 to 90 minutes; and the stirring speed is usually 2 to 2,000 rpm, preferably 5 to 1,000 rpm, more preferably 10 to 800 rpm.

The amount of the adhesive added is 0.1 to 5 parts by weight based on 100 parts by weight of the core particles. When the amount of the adhesive added is less than 0.1 part by weight, it may become difficult to form a sufficient amount of carbon black coat on the first carbon coat, thereby failing to form a sufficient second carbon black coat thereon. When the amount of the adhesive added is more than 5 parts by weight, the adhesion effect is already saturated and, therefore, it is unnecessary and meaningless to add such a large amount of the adhesive.

The mixing and stirring conditions upon adhesion of the second carbon black coat may be appropriately selected such that the carbon black can be uniformly adhered to the adhesive. More specifically, the treating conditions may be adequately controlled such that the linear load is usually 2 to 200 Kg/cm, preferably 10 to 150 Kg/cm, more preferably 15 to 100 Kg/cm the treating time is 5 to 120 minutes, preferably 10 to 90 minutes; and the stirring speed is usually 2 to 2,000 rpm, preferably 5 to 1,000 rpm.

The amount of carbon black fine particles added for forming the second carbon black coat is 1 to 30 parts by weight based on 100 parts by weight of the core particles. When the amount of the carbon black fine particles added is

less than 1 part by weight, the amount of carbon black adhered onto the surface of the adhesive is too small, so that the adhesive may be exposed to the surface of each particle, and it is difficult to improve the absorption amount of myristic acid. Further, the dispersibility thereof is deteriorated and it is difficult to lower volume resistivity thereof. When the amount of the carbon black fine particles added is more than 30 parts by weight, the obtained black magnetic acicular composite particles tend to suffer from desorption of carbon black from the surfaces thereof, resulting in deteriorated dispersibility in vehicle.

The temperature used in the drying or heat-treatment, is preferably 40 to 200°C, more preferably 60 to 150°C, and the heating time is preferably from 10 minutes to 12 hours, more preferably from 30 minutes to 3 hours. By conducting such drying or heat-treatment, the alkoxysilane can be converted into organosilane compounds.

The surface of the core particles may be coated with at least one compound selected from the group consisting of hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon, if required, in advance of mixing and stirring with the alkoxysilane compounds or the polysiloxanes.

The coating of the hydroxides of aluminum or the like may be conducted by adding an aluminum compound, a silicon compound or both the compounds to a water suspension in

which the core particles are dispersed, followed by mixing and stirring, and further adjusting the pH value of the suspension, if required, thereby coating the surfaces of the core particles with hydroxides of aluminum or the like. The thus obtained core particles coated with the hydroxides of aluminum or the like are then filtered out, washed with water, dried and pulverized. Further, the particles coated with with at least one compound selected from the group consisting of hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon may be subjected to post-treatments such as deaeration treatment and compaction treatment, if required.

As the aluminum compounds, there may be exemplified aluminum salts such as aluminum acetate, aluminum sulfate, aluminum chloride or aluminum nitrate, alkali aluminates such as sodium aluminate or the like.

The amount of the aluminum compound added is 0.01 to 50 % by weight (calculated as Al) based on the weight of the core particles. When the amount of the aluminum compound added is less than 0.01 % by weight, it may be difficult to sufficiently coat the surfaces of the core particles with hydroxides of aluminum or the like, thereby failing to improve the effective reduction of the carbon black desorption percentage. On the other hand, when the amount of the aluminum compound added is more than 20 % by weight, the coating effect is saturated and, therefore, it is meaningless to add such an excess amount of the aluminum

compound.

As the silicon compounds, there may be exemplified #3 water glass, sodium orthosilicate, sodium metasilicate or the like.

The amount of the silicon compound added is 0.01 to 50 % by weight (calculated as  $\text{SiO}_2$ ) based on the weight of the core particles. When the amount of the silicon compound added is less than 0.01 % by weight, it may be difficult to sufficiently coat the surfaces of the core particles with hydroxides of aluminum or the like, thereby failing to improve the effective reduction of the carbon black desorption percentage. On the other hand, when the amount of the silicon compound added is more than 20 % by weight, the coating effect is saturated and, therefore, it is meaningless to add such an excess amount of the silicon compound.

In the case where both the aluminum and silicon compounds are used in combination for the coating, the total amount of the aluminum and silicon compounds added is preferably 0.01 to 50 % by weight (calculated as a sum of Al and  $\text{SiO}_2$ ) based on the weight of the magnetic acicular particles.

Next, the process for producing the magnetic recording medium according to the present invention is described.

The magnetic recording medium according to the present invention can be produced by coating the surface of the non-magnetic base film with a magnetic coating composition

comprising magnetic acicular particles, a binder resin, and a solvent to form a magnetic recording layer thereon, and then magnetically orienting the magnetic recording layer.

As the solvents, there may be used methyl ethyl ketone, toluene, cyclohexanone, methyl isobutyl ketone, tetrahydrofuran, a mixture of these solvents or the like.

The total amount of the solvent used is 65 to 1,000 parts by weight based on 100 parts by weight of the magnetic acicular particles. When the amount of the solvent used is less than 65 parts by weight, the viscosity of the magnetic coating composition prepared therefrom becomes too high, thereby making it difficult to apply the magnetic coating composition. On the other hand, when the amount of the solvent used is more than 1,000 parts by weight, the amount of the solvent volatilized during the formation of the coating film becomes too large, thereby rendering the coating process industrially disadvantageous.

#### EMBODIMENT FOR CARRYING OUT THE INVENTION

The embodiment for carrying out the present invention will now be described in more detail.

The average major axial diameter and the average minor axial diameter of core particles, intermediate composite particles and magnetic acicular particles, and average particle diameter of carbon black fine particles were respectively expressed by the average of values (measured in a predetermined direction) of about 350 particles which were

sampled from a micrograph obtained by magnifying an original electron micrograph (x120,000) by four times in each of the longitudinal and transverse directions.

The aspect ratio of the particles was expressed by the ratio of average major axial diameter to average minor axial diameter thereof.

The geometrical standard deviation of major axial diameter was expressed by values obtained by the following method. That is, the major axial diameters were measured from the above magnified electron micrograph. The actual major axial diameter and the number of the particles were calculated from the measured values. On a logarithmic normal probability paper, the major axial diameters were plotted at regular intervals on the abscissa-axis and the accumulative number (under integration sieve) of particles belonging to each interval of the major axial diameter were plotted by percentage on the ordinate-axis by a statistical technique.

The major axial diameter corresponding to the number of particles of 50 % and 84.13 %, respectively, were read from the graph, and the geometrical standard deviation was calculated from the following formula:

Geometrical standard deviation =

{major axial diameter corresponding to 84.13

%

under integration sieve}/



{major axial diameter (geometrical average diameter) corresponding to 50 % under integration sieve}

The closer to 1 the geometrical standard deviation value, the more excellent the major axial diameter distribution.

The specific surface area was expressed by the value measured by a BET method.

The amount of Al, Si and Co which were present within core particles, intermediate composite particles or magnetic acicular particles, and the amount of Si contained in the organosilicon compounds which are present on the surface of intermediate composite particles or magnetic acicular particles, were measured by a fluorescent X-ray spectroscopy device 3063 M (manufactured by Rigaku Denki Kogyo Co., Ltd.) according to JIS K0119 "General rule of fluorescent X-ray analysis".

The content of Fe<sup>2+</sup> in the core particles is expressed by the value measured by the following chemical analysis method.

That is, 25 ml of a mixed solution composed of phosphoric acid and sulfuric acid at a mixing ratio of 2:1, was added to 0.5 g of core particles, thereby dissolving the core particles in the mixed solution. After several droplets of diphenylamine sulfonic acid as an indicator was added to the diluted solution, the solution was subjected to

oxidation-reduction titration using an aqueous potassium bichromate solution. The titration was terminated when the diluted solution exhibited a violet color. The amount of  $\text{Fe}^{2+}$  was measured from the amount of the aqueous potassium bichromate solution used up to the termination of the titration.

The amount of carbon black coat formed on the surface of the intermediate composite particles or magnetic acicular particles was measured by "Horiba Metal, Carbon and Sulfur Analyzer EMIA-2200 Model" (manufactured by Horiba Seisakusho Co., Ltd.).

The blackness of the core particles, intermediate composite particles, magnetic acicular particles and carbon black was measured by the following method. That is, 0.5 g of sample particles and 1.5 ml of castor oil were intimately kneaded together by a Hoover's muller to form a paste. 4.5 g of clear lacquer was added to the obtained paste and was intimately kneaded to form a paint. The obtained paint was applied on a cast-coated paper by using a 6-mil applicator to produce a coating film piece (having a film thickness of about 30  $\mu\text{m}$ ). The thus obtained coating film piece was measured according to JIS Z 8729 by a multi-light source spectrographic colorimeter MSC-IS-2D (manufactured by Suga Testing Machines Manufacturing Co., Ltd.) to determine an  $L^*$  value of colorimetric indices thereof. The blackness was expressed by the  $L^*$  value measured.

Here, the  $L^*$  value represents a lightness, and the smaller the  $L^*$  value, the more excellent the blackness.

The volume resistivity of the core particles, intermediate composite particles and the magnetic acicular particles was measured by the following method.

That is, first, 0.5 g of the sample particles to be measured was weighted, and press-molded at 140 Kg/cm<sup>2</sup> (13,720 kPa) using a KBr tablet machine (manufactured by Simazu Seisakusho Co., Ltd.), thereby forming a cylindrical test piece.

Next, the thus obtained cylindrical test piece was exposed to an atmosphere maintained at a temperature of 25°C and a relative humidity of 60 % for 12 hours. Thereafter, the cylindrical test piece was set between stainless steel electrodes, and a voltage of 15V was applied between the electrodes using a Wheatstone bridge (model 4329A, manufactured by Yokogawa-Hokushin Denki Co., Ltd.) to measure a resistance value  $R$  (•).

The cylindrical test piece was measured with respect to an upper surface area  $A$  (cm<sup>2</sup>) and a thickness  $t_0$  (cm) thereof. The measured values were inserted into the following formula, thereby obtaining a volume resistivity  $X$  (••cm).

$$X (\bullet\bullet\text{cm}) = R \times (A/t_0)$$

The thickness of carbon black coat formed on the surfaces of the magnetic acicular particles is expressed by

the value which was obtained by first measuring an average thickness of carbon black coat formed onto the surfaces of the particles on a photograph ( $\times 5,000,000$ ) obtained by magnifying (ten times) a micrograph ( $\times 500,000$ ) produced at an accelerating voltage of 200 kV using a transmission-type electron microscope (JEM-2010, manufactured by Japan Electron Co., Ltd.), and then calculating an actual thickness of carbon black coat formed from the measured average thickness.

The desorption percentage (%) of carbon black desorbed from the composite particles or black magnetic acicular composite particles was measured by the following method. The closer to zero the desorption percentage (T %), the smaller the amount of carbon black desorbed from the sample particles.

That is, 3 g of the sample particles and 40 ml of ethanol were placed in a 50-ml precipitation pipe and then was subjected to ultrasonic dispersion for 20 minutes. Thereafter, the obtained dispersion was allowed to stand for 120 minutes, and separated the carbon black desorbed from the sample particles on the basis of the difference in specific gravity therebetween. Next, the thus separated sample particles were mixed again with 40 ml of ethanol, and the obtained mixture was further subjected to ultrasonic dispersion for 20 minutes. Thereafter, the obtained dispersion was allowed to stand for 120 minutes, thereby separating the sample particles and carbon black desorbed,

from each other. The thus separated black magnetic acicular composite particles were dried at 100°C for one hour, and then the carbon content thereof was measured by the "Horiba Metal, Carbon and Sulfur Analyzer EMIA-2200 Model" (manufactured by HORIBA SEISAKUSHO CO., LTD.). The desorption percentage (T %) was calculated according to the following formula:

$$T (\%) = \{(W_a - W_e)/W_a\} \times 100$$

wherein  $W_a$  represents an amount of carbon black initially formed on the sample particles; and  $W_e$  represents an amount of carbon black which still remains on the sample particles after the above desorption test.

The viscosity of the coating composition was obtained by measuring the viscosity of the coating composition at 25°C at a shear rate  $D$  of  $1.92 \text{ sec}^{-1}$  by using "E type viscometer EMD-R" (manufactured by Tokyo Keiki, Co., Ltd.).

The gloss of the surface of the coating film of the magnetic recording layer was measured at an angle of incidence of 45° by "glossmeter UGV-5D" (manufactured by Suga Shikenki, Co., Ltd.).

The surface roughness  $R_a$  is expressed by the average value of the center-line average roughness of the profile curve of the surface of the coating film of the magnetic recording layer by using "Surfcom-575A" (manufactured by

Tokyo Seimitsu Co., Ltd.).

The strength of the coating film was expressed the Young's modulus obtained by "Autograph" (produced by Shimazu Seisakusho Co., Ltd.). The Young's modulus was expressed by the ratio of the Young's modulus of the coating film to that of a commercially available video tape "AV T-120" (produce by Victor Company of Japan, Limited). The higher the relative value, the more favorable.

The magnetic properties of the core particles, intermediate composite particles, the magnetic acicular particles and magnetic recording medium were measured under an external magnetic field of 10 kOe by "Vibration Sample Magnetometer VSM-3S-15 (manufactured by Toei Kogyo, Co., Ltd.)".

The light transmittance is expressed by the linear adsorption coefficient calculated by substituting the light transmittance measured by using "UV-Vis Recording Spectrophotometer UV-2100" (manufactured by Shimazu Seisakusho, Ltd.) for the following formula. The larger the value, the more difficult it is for the magnetic recording medium to transmit light:

Linear adsorption coefficient ( $\mu\text{m}^{-1}$ ) =  $\{1 \ln (1/t)\}/FT$   
wherein  $t$  represents a light transmittance (-) at  $\lambda = 900$  nm, and  $FT$  represents thickness ( $\mu\text{m}$ ) of the coating film used for the measurement.

The surface electrical resistivity of the coating film of the magnetic recording layer was measured by the following method. That is, the coating film to be measured was exposed to the environment maintained at a temperature of 25°C and a relative humidity of 60 %, for not less than 12 hours. Thereafter, the coating film was slit into 6 mm width, and the slit coating film was placed on two metal electrodes having a width of 6.5 mm such that a coating surface thereof was contacted with the electrodes. 1.7 N (170 gw) were respectively suspended at opposite ends of the coating film so as to bring the coating film into close contact with the electrodes. D.C. 500 V was applied between the electrodes, thereby measuring the surface electrical resistivity of the coating film.

The friction coefficient of the magnetic recording medium was determined by measuring a frictional force between a surface of the magnetic tape and a metal surface (aluminum polished surface) using a tensile tester TENSILON (manufactured by Shimadzu Seisakusho Co., Ltd.), and expressed by the ratio of the measured value to the load.

The running durability was evaluated by the actual operating time under the conditions that the load was 1.96 N (200 gw) and the relative speed of the head and the tape was 16 m/s by using "Media Durability Tester MDT-3000" (manufactured by Steinberg Associates). The longer the actual operating time, the higher the running durability.

The thickness of each of the non-magnetic base film and the magnetic recording layer constituting the magnetic recording medium was measured in the following manner by using "Digital Electronic Micrometer R351C" (manufactured by Anritsu Corp.).

The thickness (A) of the non-magnetic base film was first measured by a digital electron micrometer "K351C" (manufactured by Anritsu Denki Co., Ltd.). After forming a magnetic recording layer on the non-magnetic base film, a thickness (B) of the thus obtained magnetic recording medium (a total thickness of the non-magnetic base film and the magnetic recording layer) was measured by the same method as used above. Then, the thickness of the magnetic recording layer is obtained by subtracting (A) from (B).

<Production of magnetic acicular particles>

20 kg of acicular cobalt-coated magnetite particles (cobalt content: 2.38 % by weight based on the weight of the acicular cobalt-coated magnetite particles;  $\text{Fe}^{2+}$  content: 15.5 % by weight based on the weight of the acicular cobalt-coated magnetite particles; average major axis diameter:  $0.264 \mu\text{m}$ ; average minor axis diameter:  $0.0334 \mu\text{m}$ ; aspect ratio: 7.9:1; geometrical standard deviation value: 1.36; BET specific surface area value:  $37.8 \text{ m}^2/\text{g}$ ; blackness ( $L^*$  value): 22.8; volume resistivity:  $6.8 \times 10^7 \text{ } \Omega\cdot\text{cm}$ ; myristic acid absorption:  $0.78 \text{ mg/m}^2$ ; coercive force value: 683 Oe saturation magnetization value:  $81.3 \text{ emu/g}$ ), were



deagglomerated in 150 liters of pure water using a stirrer, and further passed through a "TK pipeline homomixer" (tradename, manufactured by Tokushu Kika Kogyo Co., Ltd.) three times, thereby obtaining a slurry containing the acicular cobalt-coated magnetite particles.

Successively, the obtained slurry containing the acicular cobalt-coated magnetite particles was passed through a transverse-type sand grinder (tradename "MIGHTY MILL MHG-1.5L", manufactured by Inoue Seisakusho Co., Ltd.) five times at an axis-rotating speed of 2,000 rpm, thereby obtaining a slurry in which the acicular cobalt-coated magnetite particles were dispersed.

The particles in the obtained slurry which remained on a sieve of 325 meshes (mesh size: 44  $\mu\text{m}$ ) was 0 %. The slurry was filtered and washed with water, thereby obtaining a filter cake containing the acicular cobalt-coated magnetite particles. After the obtained filter cake containing the acicular cobalt-coated magnetite particles was dried at 120°C, 11.0 kg of the dried particles were then charged into an edge runner "MPUV-2 Model" (tradename, manufactured by Matsumoto Chuzo Tekkosho Co., Ltd.), and mixed and stirred at 30 Kg/cm and a stirring speed of 22 rpm for 15 minutes, while introducing nitrogen gas thereinto at a rate of 2 liter/minute, thereby lightly deagglomerating the particles.

220 g of methyltriethoxysilane (tradename: "TSL8123", produced by GE TOSHIBA SILICONE CO., LTD.) was mixed and

diluted with 200 ml of ethanol to obtain a methyltriethoxysilane solution. The methyltriethoxysilane solution was added to the deagglomerated acicular cobalt-coated magnetite particles under the operation of the edge runner. The acicular cobalt-coated magnetite particles were continuously mixed and stirred at a linear load of 30 Kg/cm and a stirring speed of 22 rpm for 20 minutes.

Next, 550 g of carbon black fine particles A (particle shape: granular shape; average particle size:  $0.022\ \mu\text{m}$ ; geometrical standard deviation value: 1.68; BET specific surface area value:  $134\ \text{m}^2/\text{g}$ ; and blackness ( $L^*$  value): 16.6; pH value: 3.4; DBP oil absorption: 89 ml/100 g) were added to the acicular cobalt-coated magnetite particles coated with methyltriethoxysilane for 10 minutes while operating the edge runner. Further, the mixed particles were continuously stirred at a linear load of 30 Kg/cm and a stirring speed of 22 rpm for 30 minutes to form the carbon black coat on the coating layer composed of methyltriethoxysilane, thereby obtaining composite particles.

In order to determine the coating amount of methyltriethoxysilane and the amount of carbon black adhered, a part of the obtained composite particles were sampled and aged at  $105^\circ\text{C}$  for 60 minutes using a dryer. As a result, it was confirmed that the coating amount of methyltriethoxysilane was 0.29 % by weight (calculated as Si), and the amount of carbon black adhered was 4.73 % by

weight (corresponding to 5 parts by weight based on 100 parts by weight of the core particles). Further, as a result of the observation of electron micrograph, it was confirmed that almost whole amount of carbon black added was adhered onto the coating layer of organosilane compounds produced from methyltriethoxysilane.

Next, 220 g of dimethyl polysiloxane was added to the composite particles while operating an edge runner, and the obtained mixture was then mixed and stirred at a linear load of 60 Kg/cm for 30 minutes, thereby obtaining composite particles on the surfaces of which dimethyl polysiloxane was uniformly adhered. The stirring speed used in the above treatment was 22 rpm.

Next, 1,650 g of the above carbon black fine particles A were added to the above obtained intermediate composite particles for 10 minutes while operating the edge runner. Then, these particles were mixed and stirred with each other at a linear load of 60 Kg/cm for 30 minutes to form the second carbon black coat onto the surface of the first carbon black coat through dimethyl polysiloxane as an adhesive, thereby obtaining magnetic acicular particles. The stirring speed used in the above treatment was 22 rpm.

The obtained magnetic acicular particles were heat-treated at 80°C for 120 minutes by using a. As shown in the electron micrograph, the resultant magnetic acicular particles had an average major axis diameter of 0.267  $\mu\text{m}$ , an average minor axis diameter of 0.0340  $\mu\text{m}$ , an aspect ratio of

7.9:1. In addition, the magnetic acicular particles showed a geometrical standard deviation value of 1.36, a BET specific surface area value of  $40.5 \text{ m}^2/\text{g}$ , a blackness ( $L^*$  value) of 18.9 and a volume resistivity of  $6.4 \times 10^4 \text{ } \cdot\cdot\text{cm}$ , a myristic acid-adsorption of  $0.26 \text{ mg/m}^2$  and a carbon black desorption percentage of 7.1 %. As to the magnetic properties, the coercive force value of the magnetic acicular particles was 676 Oe and the saturation magnetization value was  $73.2 \text{ emu/g}$ .

Further, it was confirmed that the total amount of carbon black adhered and bonded was 16.58 % by weight (calculated as C; corresponding to 20.0 parts by weight based on 100 parts by weight of the core particles); and the coating amount of dimethyl polysiloxane was 0.71 % by weight (calculated as Si). Meanwhile, as a result of the observation by electron microscope, it was recognized that since substantially no liberated carbon black was observed, almost whole amount of carbon black added was adhered onto the first carbon black coat.

It was confirmed that the thickness of carbon black adhered on the surface of each particle was  $0.0017 \text{ } \mu\text{m}$ .

<Production of magnetic recording medium: Formation of magnetic recording layer>

12 g of the thus obtained magnetic acicular particles, 1.2 g of a polishing agent (AKP-30: trade name, produced by Sumitomo Chemical Co., Ltd.), 0.06 g of carbon black (#2400B, trade name, produced by Mitsubishi Chemical Corp.),

a binder resin solution (30 % by weight of vinyl chloride-vinyl acetate copolymer resin having a sodium sulfonate group and 70 % by weight of cyclohexanone) and cyclohexanone were mixed to obtain a mixture (solid content: 78 % by weight). The mixture was further kneaded by a plast-mill for 30 minutes to obtain a kneaded material.

The thus-obtained kneaded material was charged into a 140 ml-glass bottle together with 95 g of 1.5 mm $\phi$  glass beads, a binder resin solution (30 % by weight of polyurethane resin having a sodium sulfonate group and 70 % by weight of a solvent (methyl ethyl ketone : toluene = 1 : 1)), cyclohexanone, methyl ethyl ketone and toluene, and the mixture was mixed and dispersed by a paint shaker for 6 hours. Then, the lubricant and hardening agent were added to the mixture, and the resultant mixture was mixed and dispersed by a paint shaker for 15 minutes.

The thus-obtained magnetic coating composition was as follows:

Magnetic acicular particles	100 parts by weight
Vinyl chloride-vinyl acetate copolymer resin having a sodium sulfonate group	10 parts by weight
Polyurethane resin having a sodium sulfonate group	10 parts by weight
Polishing agent (AKP-30)	10 parts by weight
Carbon black (#2400B)	0.5 parts by weight

Lubricant (myristic acid: butyl	
stearate = 1 : 2)	3.0 parts by weight
Hardening agent (polyisocyanate)	5.0 parts by weight
Cyclohexanone	65.8 parts by weight
Methyl ethyl ketone	164.5 parts by weight
Toluene	98.7 parts by weight

The viscosity of the obtained magnetic coating composition was 2,202 cP.

The magnetic coating composition obtained was applied to a polyethylene terephthalate film (thickness: 12  $\mu\text{m}$ ) as a non-magnetic base film to a thickness of 45  $\mu\text{m}$  by an applicator, and the magnetic recording medium obtained was oriented and dried in a magnetic field, and then calendered. The magnetic recording medium was then subjected to a curing reaction at 60°C for 24 hours, and thereafter slit into a width of 0.5 inch (1.27 cm), thereby obtaining a magnetic tape. The thickness of the respective magnetic recording layer was 3.5  $\mu\text{m}$ .

The coercive force value of the magnetic tape produced by forming a magnetic recording layer on the non-magnetic base film was 728 Oe, the squareness (Br/Bm) thereof was 0.89, the gloss thereof was 176 %, the surface roughness Ra thereof was 7.6 nm, a Young's modulus (relative value) of 136, the linear absorption coefficient thereof was 2.77  $\mu\text{m}^{-1}$ , and the surface electrical resistivity was  $1.1 \times 10^7 \text{ } \Omega/\text{cm}^2$ . Further, as to the durability of the magnetic tape, the running durability time was not less than 28.6 minutes and a

friction coefficient was 0.26.

FUNCTION:

The important point of the present invention is the fact that when carbon black coats firmly formed onto the surfaces of the core particles in an amount as large as from more than 10 to 40 parts by weight based on 100 parts by weight of the core particles, the obtained magnetic acicular particles can exhibit a well-controlled myristic acid-adsorption of 0.01 to 0.3 mg/m<sup>2</sup>.

The reason why the magnetic acicular particles of the present invention can exhibit a reduced myristic acid-adsorption, is considered as follows, though not clearly known yet. That is, due to the fact that the myristic acid-adsorption of the magnetic acicular particles cannot be reduced to not more than 0.3 mg/m<sup>2</sup> in any of the cases where the carbon black desorption percentage is more than 20% even though the amount of carbon black adhered is more than 10 parts by weight, and where the amount of carbon black adhered is not more than 10 parts by weight even though the carbon black desorption percentage is not more than 20%, as described in Comparative Examples below, it is considered that many hydroxyl groups present on the surface of the core particles are prevented from being bonded with carboxyl groups of myristic acid which show a high affinity to the hydroxyl groups, by the synergistic effect of the dense carbon black coat formed on the surfaces of the core

particles which has an adequate thickness, and dimethyl polysiloxane as adhesive.

Also, the magnetic recording medium of the present invention using the above magnetic acicular particles according to the present invention can exhibit a low friction coefficient and an excellent running durability.

The reason why the magnetic recording medium of the present invention can show a reduced friction coefficient, is considered by the present inventors as follows. That is, since the amount of myristic acid adsorbed onto the surfaces of the magnetic acicular particles which are incorporated in a large amount into a magnetic recording layer thereof, is restricted to the specified range, an appropriate amount of myristic acid can be oozed onto the surface of the magnetic recording layer in a well-controlled condition for a long period of time, thereby effectively exhibiting a lubricating function thereof.

The reason why the magnetic recording medium of the present invention can show an excellent running durability, is considered by the present inventors as follows. That is, for the same reason as described above, an appropriate amount of myristic acid can be oozed onto the surface of the magnetic recording layer in a well-controlled condition, resulting in stable running durability of the magnetic recording medium.



### EXAMPLES

The present invention is described in more detail by Examples and Comparative Examples.

#### Core particles 1 to 5:

Various core particles were prepared by known methods. The same procedure as defined in Embodiment for Carrying out the Present Invention was conducted by using the thus magnetic acicular particles, thereby obtaining deagglomerated magnetic acicular particles as core particles.

Various properties of the thus obtained magnetic acicular particles are shown in Table 1.

#### Core particles 6:

The same procedure as defined in Embodiment for Carrying out the Present Invention was conducted by using 20 kg of the deagglomerated acicular cobalt-coated maghemite particles (core particles 1) and 150 liters of water, thereby obtaining a slurry containing the acicular cobalt-coated maghemite particles. The pH value of the obtained re-dispersed slurry containing the acicular cobalt-coated maghemite particles was adjusted to 10.5 by adding an aqueous sodium hydroxide solution, and then the concentration of the slurry was adjusted to 98 g/liter by adding water thereto. After 150 liters of the slurry was heated to 60°C, 5,444 ml of a 1.0 mol/liter sodium aluminate

solution (equivalent to 1.0 % by weight (calculated as Al) based on the weight of the acicular cobalt-coated maghemite particles) was added to the slurry. After allowing the slurry to stand for 30 minutes, the pH value of the slurry was adjusted to 7.5 by adding an aqueous acetic acid solution. After further allowing the slurry to stand for 30 minutes, the slurry was subjected to filtration, washing with water, drying and pulverization, thereby obtaining the acicular cobalt-coated maghemite particles coated with hydroxides of aluminum.

Main production conditions are shown in Table 2, and various properties of the obtained acicular cobalt-coated maghemite particles are shown in Table 3.

#### Core particles 7 to 10:

The same procedure as defined in the production of the core particles 6 above, was conducted except that kind of core particles, and kind and amount of additives used in the surface treatment were varied, thereby obtaining surface-treated magnetic acicular particles.

Main production conditions are shown in Table 2, and various properties of the obtained surface-treated magnetic acicular particles are shown in Table 3.

In Table 2, "A" denotes a hydroxide of aluminum and "S" denotes an oxide of silicon.

#### <Production of intermediate composite particles>

Examples 1 to 12 and Comparative Examples 1 to 5:

The same procedure as defined in Embodiment for Carrying out the Present Invention was conducted except that kind of core particles, addition or non-addition, kind and amount of alkoxysilane, polysiloxane or silicon compound upon the coating step, edge runner treatment conditions used in the coating step, kind and amount of carbon black fine particles added in the carbon black coat forming steps and edge runner treatment conditions used in the carbon black coat forming steps, were changed variously, thereby obtaining intermediate composite particles. Various properties of the carbon black fine particles B to F used, are shown in Table 4. The essential treating conditions are shown in Table 5, and various properties of the obtained composite particles are shown in Table 6. As a result of observing the composite particles obtained in Examples 1 to 12 by an electron microscope, substantially no liberated carbon black was recognized. Therefore, it was confirmed that almost whole amount of carbon black added was adhered onto the coating layer of organosilane compounds produced from alkoxysilane, or the coating layer of polysiloxane.

Meanwhile, all the additives used in Examples 3 to 5 were polysiloxanes. Specifically, "TSF484" (tradename, produced by Toshiba Silicone Co., Ltd.) was methyl hydrogen polysiloxane; "BYK-080" (tradename, produced by BYK-Chemie Japan Co., Ltd.) was modified polysiloxane; and "TSF-4770" (tradename, produced by Toshiba Silicone Co., Ltd.) was

terminal carboxyl group-modified polysiloxane.

<Production of black magnetic acicular composite particles>

Examples 13 to 24 and Comparative Examples 6 to 12:

The same procedure as defined in Embodiment for Carrying out the Present Invention was conducted except that kind of composite particles, kind and amount of adhesive added in the bonding step, edge runner treatment conditions used in the bonding step, kind and amount of carbon black fine particles added in second carbon black coat forming steps and edge runner treatment conditions used in the second carbon black coat forming steps, were changed variously, thereby obtaining black magnetic acicular composite particles.

Meanwhile, as a result of observing the black magnetic acicular composite particles obtained in Examples 13 to 24 by an electron microscope, substantially no liberated carbon black was recognized. Therefore, it was confirmed that almost whole amount of carbon black added was adhered onto the first carbon black coat.

Main treatment conditions are shown in Table 7, and various properties of the obtained black magnetic acicular composite particles are shown in Table 8.

Examples 25 to 36 and Comparative Examples 13 to 25:

<Production of magnetic recording medium >

The same procedure as defined in Embodiment for

Carrying out the Present Invention was conducted except for varying the kind of the black magnetic acicular composite particles, thereby producing a magnetic recording medium.

The main producing conditions and various properties are shown in Tables 9 to 10.

Table 1

Core particles	Kind of core particles	Properties of core particles
		Particle shape
Core particles 1	Cobalt-coated maghemite particles (Co content: 2.65 wt. %)	Acicular
Core particles 2	Cobalt-coated maghemite particles (Co content: 4.23 wt. %)	Spindle-shaped
Core particles 3	Cobalt-coated magnetite particles (Co content: 2.22 wt. %; Fe <sup>2+</sup> content: 15.9 wt. %)	Acicular
Core particles 4	Cobalt-coated magnetite particles (Co content: 4.79 wt. %; Fe <sup>2+</sup> content: 13.7 wt. %)	Spindle-shaped
Core particles 5	Magnetic metal particles containing iron as a main component (Al content: 2.80 wt. %; Co content: 5.64 wt. %)	Spindle-shaped

Table 1 (continued)

Core particles	Properties of core particles		
	Average major axial diameter ( $\mu\text{m}$ )	Average minor axial diameter ( $\mu\text{m}$ )	Aspect ratio (-)
Core particles 1	0.273	0.0334	8.2:1
Core particles 2	0.210	0.0285	7.4:1
Core particles 3	0.291	0.0359	8.1:1
Core particles 4	0.149	0.0220	6.8:1
Core particles 5	0.125	0.0175	7.1:1

Table 1 (continued)

Core particles	Properties of core particles		
	Geometrical standard deviation value (-)	BET specific surface area value ( $\text{m}^2/\text{g}$ )	Coercive force value (Oe)
Core particles 1	1.39	36.0	690
Core particles 2	1.36	40.4	843
Core particles 3	1.42	31.3	710
Core particles 4	1.45	52.9	911
Core particles 5	1.40	53.8	1,927



Table 1 (continued)

Core particles	Properties of core particles	
	Saturation magnetization value (emu/g)	Volume resistivity value ( $\cdot\cdot\text{cm}$ )
Core particles 1	76.4	$6.5 \times 10^8$
Core particles 2	78.7	$3.6 \times 10^8$
Core particles 3	82.9	$9.2 \times 10^7$
Core particles 4	81.0	$5.1 \times 10^7$
Core particles 5	136.1	$2.1 \times 10^7$

Table 1 (continued)

Core particles	Properties of core particles	
	Blackness (L* value) (-)	Myristic acid adsorption (mg/m <sup>2</sup> )
Core particles 1	24.3	0.78
Core particles 2	25.6	0.83
Core particles 3	22.9	0.86
Core particles 4	22.8	0.88
Core particles 5	22.4	1.01

Table 2

Core particles	Kind of core particles	Surface-treatment step		
		Additives		
		Kind	Calculated as	Amount (wt. %)
Core particles 6	Core particles 1	Sodium aluminate	Al	1.0
Core particles 7	Core particles 2	Water glass #3	SiO <sub>2</sub>	0.75
Core particles 8	Core particles 3	Aluminum sulfate	Al	2.0
		Water glass #3	SiO <sub>2</sub>	0.5
Core particles 9	Core particles 4	Sodium aluminate	Al	3.0
Core particles 10	Core particles 5	Water glass #3	SiO <sub>2</sub>	5.0

Table 2 (continued)

Core particles	Surface-treatment step		
	Coating composition		
	Kind	Calculated as	Amount (wt. %)
Core particles 6	A	Al	0.98
Core particles 7	S	SiO <sub>2</sub>	0.72
Core particles 8	A	Al	1.93
	S	SiO <sub>2</sub>	0.46
Core particles 9	A	Al	2.80
Core particles 10	S	SiO <sub>2</sub>	4.74

Table 3

Core particles	Properties of surface-treated magnetic acicular particles		
	Average major axial diameter ( $\mu\text{m}$ )	Average minor axial diameter ( $\mu\text{m}$ )	Aspect ratio (-)
Core particles 6	0.273	0.0334	8.2:1
Core particles 7	0.210	0.0285	7.4:1
Core particles 8	0.292	0.0360	8.1:1
Core particles 9	0.150	0.0221	6.8:1
Core particles 10	0.126	0.0176	7.2:1

Table 3 (continued)

Core particles	Properties of surface-treated magnetic acicular particles		
	Geometrical standard deviation value (-)	BET specific surface area value ( $\text{m}^2/\text{g}$ )	Coercive force value (Oe)
Core particles 6	1.40	36.4	686
Core particles 7	1.35	40.9	834
Core particles 8	1.41	32.6	701
Core particles 9	1.45	54.8	900
Core particles 10	1.39	56.0	1,899

Table 3 (continued)

Core particles	Properties of surface-treated magnetic acicular particles	
	Saturation magnetization value (emu/g)	Volume resistivity value ( $\cdot\cdot\text{cm}$ )
Core particles 6	75.9	$7.2 \times 10^8$
Core particles 7	78.3	$4.5 \times 10^8$
Core particles 8	81.5	$1.8 \times 10^8$
Core particles 9	79.8	$8.6 \times 10^7$
Core particles 10	133.2	$4.3 \times 10^7$

Table 3 (continued)

Core particles	Properties of surface-treated magnetic acicular particles	
	Blackness (L* value) (-)	Myristic acid adsorption (mg/m <sup>2</sup> )
Core particles 6	24.3	0.57
Core particles 7	25.6	0.63
Core particles 8	23.3	0.56
Core particles 9	23.0	0.59
Core particles 10	22.6	0.76



Table 4

Kind of carbon black fine particles	Properties of carbon black fine particles		
	Particle shape	Average particle size ( $\mu\text{m}$ )	Geometrical standard deviation value (-)
Carbon black A	Granular	0.022	1.68
Carbon black B	Granular	0.022	1.78
Carbon black C	Granular	0.015	1.56
Carbon black D	Granular	0.030	2.06
Carbon black E	Granular	0.024	1.69
Carbon black F	Granular	0.028	1.71

Table 4 (continued)

Kind of carbon black fine particles	Properties of carbon black fine particles			
	BET specific surface area value (m <sup>2</sup> /g)	pH value (-)	DBP oil absorption (ml/100g)	Blackness (L* value) (-)
Carbon black B	133.5	3.4	84	14.6
Carbon black C	265.3	3.7	57	15.2
Carbon black D	84.6	8.0	95	17.0
Carbon black E	113.6	10.8	102	16.2
Carbon black F	800.0	7.0	200	15.3

Table 5

Examples and Comparative Examples	Kind of core particles	Production of composite particles	
		Coating step with alkoxyasilane, polysiloxane or silicon compound	
		Additives	
		Kind	Amount added (part by weight)
Example 1	Core particles 1	Methyl triethoxysilane	2.0
Example 2	Core particles 2	Methyl trimethoxysilane	1.0
Example 3	Core particles 3	TSF484	1.0
Example 4	Core particles 4	BYK-080	1.0
Example 5	Core particles 5	TSF4770	1.0
Example 6	Core particles 6	Methyl triethoxysilane	2.0
Example 7	Core particles 7	Methyl trimethoxysilane	1.5
Example 8	Core particles 8	Dimethyl dimethoxysilane	3.0
Example 9	Core particles 9	Phenyl triethoxysilane	5.0
Example 10	Core particles 10	Isobutyl trimethoxysilane	1.0
Example 11	Core particles 1	Methyl triethoxysilane	1.0
Example 12	Core particles 1	Methyl triethoxysilane	1.0
Comparative Example 1	Core particles 1	-	-
Comparative Example 2	Core particles 1	Methyl triethoxysilane	0.005
Comparative Example 3	Core particles 1	Methyl triethoxysilane	1.0
Comparative Example 4	Core particles 1	$\gamma$ -aminopropyl triethoxysilane	1.0
Comparative Example 5	Core particles 1	-	-

Table 5 (continued)

Examples and Comparative Examples	Production of composite particles		
	Coating step with alkoxysilane, polysiloxane or silicon compound		
	Edge runner treatment		Coating amount (calculated as Si) (wt. %)
	Linear load (Kg/cm)	Time (min.)	
Example 1	60	30	0.28
Example 2	30	30	0.19
Example 3	45	20	0.42
Example 4	60	30	0.17
Example 5	45	20	0.35
Example 6	30	30	0.29
Example 7	60	30	0.29
Example 8	60	20	0.65
Example 9	45	30	0.66
Example 10	60	20	0.14
Example 11	30	20	0.15
Example 12	30	20	0.15
Comparative Example 1	-	-	-
Comparative Example 2	30	20	$7 \times 10^{-4}$
Comparative Example 3	30	20	0.15
Comparative Example 4	30	20	0.13
Comparative Example 5	-	-	-

Table 5 (continued)

Examples and Comparative Examples	Production of composite particles	
	Coat formation step with carbon black	
	Carbon black	
	Kind	Amount added (part by weight)
Example 1	B	3.0
Example 2	B	10.0
Example 3	C	5.0
Example 4	C	5.0
Example 5	D	10.0
Example 6	D	5.0
Example 7	B	7.5
Example 8	C	5.0
Example 9	D	3.0
Example 10	B	10.0
Example 11	E	7.5
Example 12	F	7.5
Comparative Example 1	B	5.0
Comparative Example 2	C	5.0
Comparative Example 3	D	15.0
Comparative Example 4	D	5.0
Comparative Example 5	D	10.0

Table 5 (continued)

Examples and Comparative Examples	Production of composite particles		
	Coat formation step with carbon black		
	Edge runner treatment		Amount adhered (calculated as C) (wt. %)
	Linear load (Kg/cm)	Time (min.)	
Example 1	60	20	2.85
Example 2	30	30	9.06
Example 3	45	30	4.75
Example 4	60	30	4.72
Example 5	30	20	9.08
Example 6	45	30	4.74
Example 7	60	30	6.94
Example 8	30	20	4.75
Example 9	45	30	2.86
Example 10	60	30	9.00
Example 11	60	30	6.96
Example 12	60	30	6.83
Comparative Example 1	30	20	4.74
Comparative Example 2	30	20	4.73
Comparative Example 3	30	20	13.01
Comparative Example 4	30	20	4.68
Comparative Example 5	30	20	9.08

Table 6

Examples and Comparative Examples	Properties of composite particles		
	Average major axial diameter ( $\mu\text{m}$ )	Average minor axial diameter ( $\mu\text{m}$ )	Aspect ratio (-)
Example 1	0.274	0.0336	8.2:1
Example 2	0.212	0.0289	7.3:1
Example 3	0.291	0.0360	8.1:1
Example 4	0.150	0.0222	6.8:1
Example 5	0.127	0.0179	7.1:1
Example 6	0.274	0.0336	8.2:1
Example 7	0.212	0.0288	7.4:1
Example 8	0.293	0.0362	8.1:1
Example 9	0.150	0.0221	6.8:1
Example 10	0.128	0.0180	7.1:1
Example 11	0.274	0.0337	8.1:1
Example 12	0.274	0.0337	8.1:1
Comparative Example 1	0.273	0.0334	8.2:1
Comparative Example 2	0.273	0.0334	8.2:1
Comparative Example 3	0.275	0.0338	8.1:1
Comparative Example 4	0.273	0.0334	8.2:1
Comparative Example 5	0.273	0.0334	8.2:1

Table 6 (continued)

Examples and Comparative Examples	Properties of composite particles		
	Geometrical standard deviation value (-)	BET specific surface area value (m <sup>2</sup> /g)	Coercive force value (Oe)
Example 2	1.40	38.0	680
Example 3	1.36	43.6	836
Example 4	1.43	32.8	700
Example 5	1.44	55.3	901
Example 6	1.39	56.4	1,908
Example 7	1.40	38.6	679
Example 8	1.36	43.1	828
Example 9	1.43	33.9	696
Example 10	1.44	55.2	892
Example 11	1.39	59.0	1,889
Example 12	1.40	38.6	679
Example 13	1.40	38.7	676
Comparative Example 1	-	41.8	678
Comparative Example 2	-	40.2	679
Comparative Example 3	-	42.9	672
Comparative Example 4	-	41.1	678
Comparative Example 5	-	45.6	674



Table 6 (continued)

Examples and Comparative Examples	Properties of composite particles		
	Saturation magnetization value (emu/g)	Volume resistivity value ( $\cdot\cdot\text{cm}$ )	Blackness ( $L^*$ value) (-)
Example 1	72.8	$4.8 \times 10^4$	19.6
Example 2	73.6	$9.6 \times 10^4$	19.1
Example 3	79.8	$8.3 \times 10^5$	20.1
Example 4	78.1	$4.6 \times 10^5$	19.8
Example 5	131.6	$2.3 \times 10^5$	19.1
Example 6	72.5	$2.6 \times 10^4$	19.7
Example 7	73.4	$7.3 \times 10^4$	19.6
Example 8	78.8	$5.1 \times 10^5$	19.4
Example 9	77.3	$1.1 \times 10^5$	19.6
Example 10	130.0	$2.4 \times 10^5$	18.5
Example 11	72.6	$3.1 \times 10^4$	19.8
Example 12	72.5	$2.2 \times 10^4$	20.1
Comparative Example 1	72.5	$6.3 \times 10^7$	22.6
Comparative Example 2	72.6	$5.1 \times 10^7$	22.8
Comparative Example 3	72.3	$9.6 \times 10^6$	19.4
Comparative Example 4	72.8	$5.4 \times 10^7$	22.5
Comparative Example 5	72.4	$1.6 \times 10^7$	22.0

Table 6 (continued)

Examples and Comparative Examples	Properties of composite particles	
	Myristic acid adsorption (mg/m <sup>2</sup> )	Carbon black desorption percentage (%)
Example 1	0.44	8.4
Example 2	0.41	8.8
Example 3	0.46	7.2
Example 4	0.48	7.9
Example 5	0.50	8.9
Example 6	0.39	3.9
Example 7	0.37	4.2
Example 8	0.38	3.6
Example 9	0.39	2.8
Example 10	0.40	4.4
Example 11	0.51	9.1
Example 12	0.49	9.6
Comparative Example 1	0.66	65.2
Comparative Example 2	0.67	46.6
Comparative Example 3	0.54	28.3
Comparative Example 4	0.71	52.8
Comparative Example 5	0.60	68.3

Table 7

Examples and Comparative Examples	Kind of core particles	Production of black magnetic acicular composite particles	
		Treating step with dimethyl polysiloxane or silicon compound	
		Additives	
		Kind	Amount added (part by weight)
Example 13	Example 1	Dimethylpolysiloxane	1.0
Example 14	Example 2	Dimethylpolysiloxane	1.5
Example 15	Example 3	Dimethylpolysiloxane	2.0
Example 16	Example 4	Dimethylpolysiloxane	1.5
Example 17	Example 5	Dimethylpolysiloxane	2.0
Example 18	Example 6	Dimethylpolysiloxane	1.5
Example 19	Example 7	Dimethylpolysiloxane	1.5
Example 20	Example 8	Dimethylpolysiloxane	2.0
Example 21	Example 9	Dimethylpolysiloxane	3.0
Example 22	Example 10	Dimethylpolysiloxane	1.0
Example 23	Example 11	Dimethylpolysiloxane	2.0
Example 24	Example 12	Dimethylpolysiloxane	3.0
Comparative Example 6	Comparative Example 1	Dimethylpolysiloxane	1.0
Comparative Example 7	Comparative Example 2	Dimethylpolysiloxane	1.0
Comparative Example 8	Comparative Example 3	Dimethylpolysiloxane	1.0
Comparative Example 9	Comparative Example 4	Dimethylpolysiloxane	1.0
Comparative Example 10	Example 1	-	-
Comparative Example 11	Example 1	Dimethylpolysiloxane	0.005
Comparative Example 12	Example 1	Methyltriethoxysilane	1.0

Table 7 (continued)

Examples and Comparative Examples	Production of black magnetic acicular composite particles		
	Treating step with dimethyl polysiloxane or silicon compound		
	Edge runner treatment		Coating amount (calculated as Si) (wt. %)
	Linear load (Kg/cm)	Time (min.)	
Example 13	60	30	0.31
Example 14	60	30	0.54
Example 15	30	20	0.70
Example 16	60	30	0.53
Example 17	60	20	0.72
Example 18	45	30	0.51
Example 19	75	45	0.51
Example 20	60	30	0.71
Example 21	60	25	1.01
Example 22	30	30	0.30
Example 23	30	20	0.72
Example 24	60	30	0.99
Comparative Example 6	60	30	0.31
Comparative Example 7	60	30	0.30
Comparative Example 8	60	30	0.30
Comparative Example 9	60	30	0.31
Comparative Example 10	-	-	-
Comparative Example 11	30	20	$2 \times 10^{-3}$
Comparative Example 12	30	20	0.15

Table 7 (continued)

Examples and Comparative Examples	Production of black magnetic acicular composite particles	
	Coat formation step with carbon black	
	Carbon black	
	Kind	Amount added (part by weight)
Example 13	B	10.0
Example 14	C	15.0
Example 15	D	20.0
Example 16	B	10.0
Example 17	C	10.0
Example 18	D	15.0
Example 19	B	10.0
Example 20	C	10.0
Example 21	D	20.0
Example 22	B	10.0
Example 23	E	10.0
Example 24	F	10.0
Comparative Example 6	B	10.0
Comparative Example 7	C	10.0
Comparative Example 8	D	10.0
Comparative Example 9	D	10.0
Comparative Example 10	B	10.0
Comparative Example 11	B	10.0
Comparative Example 12	B	10.0

Table 7 (continued)

Examples and Comparative Examples	Production of black magnetic acicular composite particles		
	Coat formation step with carbon black		
	Edge runner treatment		Amount adhered (calculated as C) (wt. %)
	Linear load (Kg/cm)	Time (min.)	
Example 13	60	30	9.06
Example 14	60	30	13.03
Example 15	45	30	16.45
Example 16	45	20	9.01
Example 17	60	30	9.05
Example 18	60	30	13.00
Example 19	30	20	9.00
Example 20	60	30	9.06
Example 21	60	30	16.48
Example 22	45	20	9.00
Example 23	30	30	9.01
Example 24	60	30	9.03
Comparative Example 6	45	30	9.08
Comparative Example 7	60	30	9.00
Comparative Example 8	45	30	9.03
Comparative Example 9	60	30	9.02
Comparative Example 10	60	30	9.01
Comparative Example 11	60	30	9.00
Comparative Example 12	60	30	9.05

Table 8

Examples and Comparative Examples	Properties of black magnetic acicular composite particles		
	Average major axial diameter ( $\mu\text{m}$ )	Average minor axial diameter ( $\mu\text{m}$ )	Aspect ratio (-)
Example 13	0.276	0.0340	8.1:1
Example 14	0.214	0.0295	7.3:1
Example 15	0.294	0.0368	8.0:1
Example 16	0.152	0.0226	6.7:1
Example 17	0.129	0.0174	7.4:1
Example 18	0.277	0.0341	8.1:1
Example 19	0.214	0.0292	7.3:1
Example 20	0.295	0.0367	8.0:1
Example 21	0.154	0.0229	6.7:1
Example 22	0.130	0.0183	7.1:1
Example 23	0.276	0.0341	8.1:1
Example 24	0.276	0.0340	8.1:1
Comparative Example 6	0.274	0.0336	8.2:1
Comparative Example 7	0.274	0.0336	8.2:1
Comparative Example 8	0.276	0.0340	8.1:1
Comparative Example 9	0.274	0.0336	8.2:1
Comparative Example 10	0.274	0.0336	8.2:1
Comparative Example 11	0.274	0.0336	8.2:1
Comparative Example 12	0.275	0.0338	8.1:1

Table 8 (continued)

Examples and Comparative Examples	Properties of black magnetic acicular composite particles		
	Geometrical standard deviation value (-)	BET specific surface area value (m <sup>2</sup> /g)	Coercive force value (Oe)
Example 13	1.40	39.8	672
Example 14	1.36	46.5	826
Example 15	1.43	36.3	690
Example 16	1.44	57.6	893
Example 17	1.39	58.9	1,896
Example 18	1.40	41.3	670
Example 19	1.36	45.3	821
Example 20	1.43	35.9	689
Example 21	1.44	59.1	883
Example 22	1.39	60.3	1,880
Example 23	1.40	40.1	671
Example 24	1.40	39.9	668
Comparative Example 6	-	45.6	668
Comparative Example 7	-	44.8	669
Comparative Example 8	-	46.3	666
Comparative Example 9	-	45.2	668
Comparative Example 10	-	42.3	670
Comparative Example 11	-	42.2	670
Comparative Example 12	-	41.6	671



Table 8 (continued)

Examples and Comparative Examples	Properties of black magnetic acicular composite particles		
	Saturation magnetization value (emu/g)	Volume resistivity value ( $\cdot\cdot\text{cm}$ )	Blackness (L* value) (-)
Example 13	70.3	$5.9 \times 10^3$	18.6
Example 14	71.6	$9.8 \times 10^3$	18.1
Example 15	78.0	$7.3 \times 10^4$	18.9
Example 16	76.8	$6.5 \times 10^4$	18.8
Example 17	126.5	$4.1 \times 10^4$	18.3
Example 18	69.8	$4.8 \times 10^3$	19.0
Example 19	70.1	$8.0 \times 10^3$	18.6
Example 20	76.6	$6.5 \times 10^4$	18.6
Example 21	76.0	$2.1 \times 10^4$	19.1
Example 22	125.6	$4.1 \times 10^4$	17.9
Example 23	70.3	$3.1 \times 10^3$	19.2
Example 24	71.6	$1.3 \times 10^3$	19.4
Comparative Example 6	70.6	$6.8 \times 10^6$	21.8
Comparative Example 7	70.3	$6.6 \times 10^6$	22.0
Comparative Example 8	70.1	$2.2 \times 10^6$	19.0
Comparative Example 9	70.3	$7.6 \times 10^6$	22.0
Comparative Example 10	69.8	$3.3 \times 10^4$	19.3
Comparative Example 11	69.9	$3.1 \times 10^4$	19.2
Comparative Example 12	70.1	$1.2 \times 10^4$	19.0

Table 8 (continued)

Examples and Comparative Examples	Properties of black magnetic acicular composite particles	
	Myristic acid adsorption (mg/m <sup>2</sup> )	Carbon black desorption percentage (%)
Example 13	0.24	7.1
Example 14	0.22	7.5
Example 15	0.27	7.7
Example 16	0.25	6.8
Example 17	0.28	6.9
Example 18	0.21	4.1
Example 19	0.23	3.6
Example 20	0.22	3.5
Example 21	0.23	4.4
Example 22	0.24	3.1
Example 23	0.29	8.8
Example 24	0.28	9.2
Comparative Example 6	0.33	30.4
Comparative Example 7	0.34	24.2
Comparative Example 8	0.38	21.8
Comparative Example 9	0.44	26.3
Comparative Example 10	0.46	51.8
Comparative Example 11	0.42	37.5
Comparative Example 12	0.39	21.0

Table 9

Examples	Production of magnetic recording medium		Properties of coating composition
	Kind of black magnetic composite acicular particles	Weight ratio of particles to resin (-)	Viscosity (cP)
Example 25	Example 13	5.0:1	2,560
Example 26	Example 14	5.0:1	2,283
Example 27	Example 15	5.0:1	2,682
Example 28	Example 16	5.0:1	2,713
Example 29	Example 17	5.0:1	3,830
Example 30	Example 18	5.0:1	1,968
Example 31	Example 19	5.0:1	1,832
Example 32	Example 20	5.0:1	1,963
Example 33	Example 21	5.0:1	1,932
Example 34	Example 22	5.0:1	3,603
Example 35	Example 23	5.0:1	2,202
Example 36	Example 24	5.0:1	2,560

Table 9 (continued)

Examples	Properties of magnetic recording medium		
	Thickness of magnetic layer ( $\mu\text{m}$ )	Coercive force value (Oe)	Squareness (Br/Bm) (-)
Example 25	3.5	721	0.87
Example 26	3.6	846	0.88
Example 27	3.5	703	0.88
Example 28	3.2	911	0.87
Example 29	3.8	1,963	0.87
Example 30	3.5	726	0.89
Example 31	3.3	848	0.89
Example 32	3.4	706	0.89
Example 33	3.5	910	0.90
Example 34	3.3	1,953	0.89
Example 35	3.6	716	0.88
Example 36	3.6	721	0.88

Table 9 (continued)

Examples	Properties of magnetic recording medium		
	Gloss (%)	Surface roughness Ra (nm)	Young's modulus (relative value)
Example 25	171	8.6	138
Example 26	178	7.3	134
Example 27	181	7.0	136
Example 28	176	8.1	132
Example 29	196	6.9	131
Example 30	176	7.2	141
Example 31	183	7.3	137
Example 32	188	7.0	141
Example 33	181	7.8	136
Example 34	206	8.3	136
Example 35	171	8.3	135
Example 36	173	8.3	134

Table 9 (continued)

Examples	Properties of magnetic recording medium	
	Linear absorption ( $\mu\text{m}^{-1}$ )	Friction coefficient (-)
Example 25	2.63	0.28
Example 26	3.11	0.26
Example 27	2.63	0.28
Example 28	2.80	0.27
Example 29	2.86	0.28
Example 30	2.63	0.22
Example 31	2.71	0.23
Example 32	2.78	0.23
Example 33	2.78	0.24
Example 34	3.18	0.24
Example 35	2.59	0.30
Example 36	2.61	0.29

Table 9 (continued)

Examples	Properties of magnetic recording medium	
	Running durability (min.)	Surface electrical resistivity value ( $\bullet/\text{cm}^2$ )
Example 25	26.8	$2.9 \times 10^6$
Example 26	27.6	$6.1 \times 10^6$
Example 27	26.3	$9.1 \times 10^6$
Example 28	26.9	$1.6 \times 10^7$
Example 29	26.8	$8.8 \times 10^6$
Example 30	•30	$1.7 \times 10^6$
Example 31	•30	$5.6 \times 10^6$
Example 32	•30	$8.1 \times 10^6$
Example 33	28.4	$1.2 \times 10^7$
Example 34	29.2	$2.2 \times 10^7$
Example 35	25.8	$1.3 \times 10^6$
Example 36	26.6	$1.0 \times 10^6$

Table 10

Comparative Examples	Production of magnetic recording medium		Properties of coating composition
	Kind of magnetic particles	Weight ratio of particles to resin (-)	Viscosity (cP)
Comparative Example 13	Core particles 1	5.0:1	2,813
Comparative Example 14	Core particles 2	5.0:1	2,762
Comparative Example 15	Core particles 3	5.0:1	2,733
Comparative Example 16	Core particles 4	5.0:1	2,861
Comparative Example 17	Core particles 5	5.0:1	5,206
Comparative Example 18	Comparative Example 5	5.0:1	5,260
Comparative Example 19	Comparative Example 6	5.0:1	4,603
Comparative Example 20	Comparative Example 7	5.0:1	3,812
Comparative Example 21	Comparative Example 8	5.0:1	4,163
Comparative Example 22	Comparative Example 9	5.0:1	5,163
Comparative Example 23	Comparative Example 10	5.0:1	3,362
Comparative Example 24	Comparative Example 11	5.0:1	3,233
Comparative Example 25	Comparative Example 12	5.0:1	3,168



Table 10 (continued)

Comparative Examples	Properties of magnetic recording medium		
	Thickness of magnetic layer ( $\mu\text{m}$ )	Coercive force value (Oe)	Squareness (Br/Bm) (-)
Comparative Example 13	3.6	726	0.85
Comparative Example 14	3.5	841	0.85
Comparative Example 15	3.5	706	0.84
Comparative Example 16	3.5	916	0.85
Comparative Example 17	3.8	1,996	0.87
Comparative Example 18	3.6	714	0.79
Comparative Example 19	3.5	713	0.83
Comparative Example 20	3.6	718	0.82
Comparative Example 21	3.7	712	0.81
Comparative Example 22	3.7	716	0.81
Comparative Example 23	3.5	709	0.83
Comparative Example 24	3.5	711	0.82
Comparative Example 25	3.5	713	0.82

Table 10 (continued)

Comparative Examples	Properties of magnetic recording medium		
	Gloss (%)	Surface roughness Ra (nm)	Young's modulus (relative value)
Comparative Example 13	165	10.4	134
Comparative Example 14	166	10.4	133
Comparative Example 15	162	10.8	134
Comparative Example 16	167	11.2	132
Comparative Example 17	195	13.6	129
Comparative Example 18	138	21.2	123
Comparative Example 19	155	15.3	126
Comparative Example 20	158	14.6	126
Comparative Example 21	159	13.8	125
Comparative Example 22	156	14.0	126
Comparative Example 23	143	18.3	124
Comparative Example 24	146	16.6	124
Comparative Example 25	151	15.3	126

Table 10 (continued)

Comparative Examples	Properties of magnetic recording medium	
	Linear absorption ( $\mu\text{m}^{-1}$ )	Friction coefficient (-)
Comparative Example 13	0.72	0.36
Comparative Example 14	0.68	0.38
Comparative Example 15	1.10	0.38
Comparative Example 16	1.02	0.36
Comparative Example 17	1.12	0.41
Comparative Example 18	1.68	0.41
Comparative Example 19	1.63	0.36
Comparative Example 20	1.61	0.37
Comparative Example 21	1.72	0.38
Comparative Example 22	1.70	0.42
Comparative Example 23	1.61	0.43
Comparative Example 24	1.62	0.41
Comparative Example 25	1.68	0.39

Table 10 (continued)

Comparative Examples	Properties of magnetic recording medium	
	Running durability (min.)	Surface electrical resistivity value ( $\bullet/\text{cm}^2$ )
Comparative Example 13	18.5	$6.9 \times 10^{12}$
Comparative Example 14	17.6	$1.8 \times 10^{13}$
Comparative Example 15	17.2	$9.2 \times 10^{11}$
Comparative Example 16	18.3	$4.1 \times 10^{11}$
Comparative Example 17	16.4	$3.6 \times 10^{11}$
Comparative Example 18	8.3	$1.6 \times 10^8$
Comparative Example 19	10.6	$8.3 \times 10^8$
Comparative Example 20	9.8	$7.2 \times 10^8$
Comparative Example 21	11.1	$1.4 \times 10^8$
Comparative Example 22	9.9	$6.9 \times 10^8$
Comparative Example 23	13.6	$4.3 \times 10^8$
Comparative Example 24	14.3	$3.6 \times 10^8$
Comparative Example 25	14.6	$3.1 \times 10^8$

EFFECT OF THE PRESENT INVENTION

Further, the magnetic acicular particles of the present invention can exhibit an excellent dispersibility in vehicle, a more excellent blackness, a lower volume resistivity value and a well-controlled myristic acid-adsorption. Therefore, when the particles are used for the production of magnetic recording medium, the obtained magnetic recording medium can exhibit a smooth surface, a more excellent blackness and a lower surface electrical resistivity value, and can be well-controlled in amount of myristic acid coated onto the surface of a magnetic recording layer. Accordingly, the magnetic acicular particles of the present invention is suitable as magnetic particles for magnetic recording media.

By using the above magnetic acicular particles, the magnetic recording medium according to the present invention can exhibit not only a smooth surface, a smaller light transmittance and a lower surface electrical resistivity value, but also a small friction coefficient and an excellent running durability. Therefore, the magnetic recording medium of the present invention is suitable as those for high-density recording.

DOCUMENT: ABSTRACT

ABSTRACT

OBJECT: It is an object of the present invention to provide magnetic acicular particles for producing a magnetic recording medium exhibiting not only a smooth surface, a smaller light transmittance and a lower surface electrical resistivity value, but also a small friction coefficient and an excellent running durability.

CONSTITUTION: Magnetic acicular particles for a magnetic recording medium, comprising black magnetic acicular composite particles having an average particle diameter of 0.051 to 0.35  $\mu\text{m}$  and an absorption amount of myristic acid of 0.01 to 0.3  $\text{mg}/\text{m}^2$ , and comprising:

as core particles, magnetic acicular cobalt-coated iron oxide particles or magnetic acicular metal particles containing iron as a main component,

a coating formed on surface of said core particles, comprising organosilane compounds obtainable from alkoxysilane compounds, or polysiloxanes, and

a carbon black adhered on at least a part of said coating in an amount of from more than 10 to 40 parts by weight based on 100 parts by weight of the core particles.



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VERIFICATION OF A TRANSLATION

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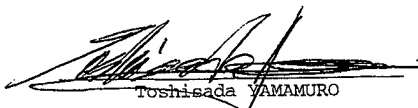
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thereon.

Date: December 19, 2003

  
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OBJECT NAME:	Abstract	1
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PROOF:	Required
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DOCUMENT NAME: SPECIFICATION

TITLE OF THE INVENTION

MAGNETIC RECORDING MEDIUM

WHAT IS CLAIMED IS:

1. A magnetic recording medium comprising:

a non-magnetic base film;

a non-magnetic undercoat layer formed on said non-magnetic base film; and

a magnetic recording layer comprising a binder resin and black magnetic acicular composite particles having an average particle diameter of 0.051 to 0.35  $\mu\text{m}$ , comprising

as core particles, magnetic acicular cobalt-coated iron oxide particles or magnetic acicular metal particles containing iron as a main component,

a coating formed on surface of said core particles, comprising organosilane compounds obtainable from alkoxysilane compounds, or polysiloxanes, and

a carbon black coat formed on said coating layer comprising said organosilicon compound, in an amount of 0.5 to 10 parts by weight based on 100 parts by weight of said core particles.

2. A magnetic recording medium comprising:

a non-magnetic base film;

a non-magnetic undercoat layer formed on said non-magnetic base film; and

a magnetic recording layer comprising a binder resin and black magnetic acicular composite particles having an average particle diameter of 0.051 to 0.35  $\mu\text{m}$ , comprising

as core particles, magnetic acicular cobalt-coated iron oxide particles or magnetic acicular metal particles containing iron as a main component,

as a lower layer, a coat formed on the surface of said core particles, comprising at least one compound selected from the group consisting of hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon

a coating formed on the lower layer, comprising organosilane compounds obtainable from alkoxysilane compounds, or polysiloxanes, and

a carbon black adhered on at least a part of said coating in an amount of from more than 10 to 40 parts by weight based on 100 parts by weight of the core.

#### DETAILED DESCRIPTION OF THE INVENTION

##### FIELD OF THE INVENTION

The object of the present invention is to provide a magnetic recording medium exhibiting a smooth surface, a smaller light transmittance and a lower surface electrical resistivity value, by using as magnetic particles magnetic acicular composite particles exhibiting not only an excellent dispersibility in vehicle due to a less amount of carbon black desorbed or fallen-off from the surfaces

thereof, but also a more excellent blackness, a lower volume resistivity value.

#### PRIOR ART

With a development of miniaturized, lightweight video or audio magnetic recording and reproducing apparatuses for long-time recording, magnetic recording media such as a magnetic tape and magnetic disk have been increasingly and strongly desired to have a higher performance, namely, a higher recording density, higher output characteristic, in particular, an improved frequency characteristic and a lower noise level.

Especially, video tapes have recently been desired more and more to have a higher picture quality, and the frequencies of carrier signals recorded in recent video tapes are higher than those recorded in conventional video tapes. In other words, the signals in the short-wave region have come to be used, and as a result, the magnetization depth from the surface of a magnetic tape has come to be remarkably small.

In order to enhance output characteristics of magnetic recording media, especially an S/N ratio thereof with respect to signals having a short wavelength, there have been demanded fineness of magnetic particles, reduction in thickness of a magnetic recording layer, high dispersibility of magnetic particles and surface smoothness of a magnetic coating film.

On the other hand, at the present time, the end position of a magnetic recording medium such as magnetic tapes has been detected by sensing a high light transmittance portion of the magnetic recording medium by means of a video deck. In the case where the particle size of magnetic particles dispersed in the magnetic recording layer become finer and the thickness of the magnetic recording medium is reduced in order to meet the requirement for high performance of the magnetic recording medium as described hereinbefore, the magnetic recording medium shows a high light transmittance as a whole, so that it has been difficult to detect the end position thereof by means of the video deck. In order to solve this problem, carbon black fine particles have been added to the magnetic recording layer in an amount of usually about 6 to 12 parts by weight based on 100 parts by weight of the magnetic particles, thereby reducing the light transmittance of the magnetic recording medium. For this reason, in current videotapes, it is essential to add carbon black fine particles, etc., to the magnetic recording layer thereof.

However, when a large amount of such non-magnetic carbon black fine particles are added to the magnetic recording layer, the magnetic recording medium suffers from deterioration in signal recording property, thereby hindering high-density recording thereon, and the reduction in thickness of the magnetic recording layer becomes incapable. Further, due to the fact that the carbon black

fine particles have a large BET specific surface area value, and are deteriorated in solvent-wettability, it has been difficult to disperse these carbon black fine particles in vehicle, thereby failing to obtain a magnetic recording medium having a smooth surface.

Further, in the case where the magnetic recording medium has a high surface electrical resistivity, the electrostatic charge amount thereof is increased, so that cut chips or dusts tend to adhere onto the surface of the magnetic recording medium upon the production or use thereof, thereby causing such a problem that the dropout frequently occurs. Therefore, in order to reduce not only the light transmittance of the magnetic recording medium but also the surface electrical resistivity thereof, especially below about  $10^8 \Omega/\text{cm}^2$ , the carbon black fine particles have been conventionally added to the magnetic recording layer of the magnetic recording medium.

However, as described above, in the case where the amount of such carbon black fine particles or the like which do not contribute to magnetic properties of the magnetic recording layer, is increased, there are caused such problems that the magnetic recording medium suffers from deterioration in signal recording property, the reduction in thickness of the magnetic recording layer becomes incapable, and further the surface smoothness of the magnetic recording layer is deteriorated.

Also, since the carbon black fine particles are bulky

particles having a bulk density as low as about  $0.1 \text{ g/cm}^3$ , the handling property and workability thereof are deteriorated. In addition, it has been pointed out that the use of such carbon black fine particles causes problems concerning safety and hygiene such as carcinogenesis.

Magnetic recording media have been continuously required to enhance performances thereof. In particular, it has been strongly required to improve physical properties of these magnetic recording media such as running property in addition to the above-described high-density recording property.

The running property of magnetic recording media can be ensured by adding a fatty acid such as myristic acid or stearic acid (hereinafter referred to merely as "myristic acid") in an amount of usually about 0.5 to 5 % by weight based on the weight of magnetic particles, into a magnetic recording layer generally formed as an upper layer of the respective magnetic recording medium, and then allowing the myristic acid to be gradually oozed out on the surface of the magnetic recording layer so as to render the surface slidable.

When the amount of the myristic acid oozed out on the surface of the magnetic recording layer is too small, it is not possible to ensure a good running property of the magnetic recording media. On the contrary, when a large amount of the myristic acid is added to the magnetic recording layer so as to allow a large amount of myristic

acid to be subsequently oozed out on the surface thereof, the myristic acid is preferentially adsorbed onto the surface of each magnetic particle dispersed in the magnetic recording layer, thereby inhibiting the magnetic particles from being contacted with or adsorbed into resins. As a result, it is difficult to disperse the magnetic particles in vehicle. Also, the increase in amount of the myristic acid as a non-magnetic component causes deterioration in magnetic properties of the magnetic recording media. Further, since the myristic acid acts as a plasticizer, there arise problems such as deterioration in mechanical strength of the magnetic recording media.

Recently, with further reduction in thickness of the magnetic recording layer, the absolute amount of myristic acid added to the magnetic recording layer is decreased. In addition, since the particle size of the magnetic particles have become much finer in order to meet the requirement of high-density recording, the BET specific surface area thereof is increased, so that a large amount of myristic acid is absorbed onto the surfaces of the magnetic particles. Under these conditions, it is more and more difficult to properly adjust the amount of the myristic acid oozed out on the surface of the magnetic recording layer by the amount of the myristic acid added into the magnetic recording layer, thereby ensuring a good running property of the magnetic recording layer.

Accordingly, it is a tendency of the reduction in



thickness of the magnetic recording layer, has been strongly required to properly adjust the amount of myristic acid oozed out on the surface of the magnetic recording layer and ensure a good running property of the magnetic recording media.

In order to improve electrical resistance and running durability of the magnetic recording media, there have been proposed such magnetic particles on the surfaces of which carbon and/or graphite are deposited or adhered in an amount of 0.2 to 10.0 % by weight based on the weight of the magnetic particles (corresponding to 0.2 to 11.11 parts by weight based on 100 parts by weight of the magnetic particles) by various methods such as gas-phase growth, e.g., chemical vapor deposition (CVD) or physical vapor deposition (PVD), reduction of organic compounds, and thermal decomposition or incomplete combustion of hydrocarbons (Japanese Patent Application Laid-Open (KOKAI) No. 10-269558).

Also, hitherto, with the reduction in thicknesses of magnetic recording layer and non-magnetic base film of magnetic recording media, it has been variously attempted to impart good surface smoothness and large stiffness thereto by improving a substrate on which the magnetic recording layer is formed. For instance, there has been proposed a non-magnetic substrate composed of a non-magnetic base film and at least one undercoat layer formed on the non-magnetic base film. The undercoat layer is composed of a binder and

non-magnetic particles dispersed in the vehicle, which contain iron as a main component, e.g., acicular hematite particles or acicular iron oxide hydroxide particles (hereinafter referred to merely as "non-magnetic undercoat layer"). Such a non-magnetic substrate is already put into practice (refer to Japanese Patent Publication (KOKOKU) No. 6-93297, Japanese Patent Application Laid-Open (KOKAI) Nos. 62-159338, 63-187418, 4-167225, 4-325915, 5-73882, 5-182177, 5-347017 and 6-60362, or the like).

As non-magnetic particles for the non-magnetic undercoat layer, there have been known non-magnetic particles which are treated with a hydroxide of aluminum, an oxide of aluminum, a hydroxide of silicon or an oxide of silicon in order to improve a dispersibility of these particles in vehicle, etc., for further smoothening the surface of a substrate and increasing the stiffness thereof (Japanese Patent Nos. 2,571,350 and 2,582,051, and Japanese Patent Application Laid-Open (KOKAI) Nos. 6-60362, 9-22524 and 9-27117).

Also, in order to reduce a light transmittance of magnetic recording media by reducing the amount of carbon black added to a magnetic recording layer thereof, it has been known to use as non-magnetic particles for non-magnetic undercoat layer, blackish brown acicular hematite particles or blackish brown acicular iron oxide hydroxide particles (Japanese Patent Application Laid-Open (KOKAI) Nos. 7-66020, 8-259237 and 9-167333 or the like). Further, it has been

known to use non-magnetic acicular particles which are composed of acicular hematite particles or acicular iron oxide hydroxide particles as core particles and carbon black fine particles adhered onto the surfaces of the core particles in an amount of 1 to 20 parts by weight based on 100 parts by weight of the core particles (European Patent No. 0,824,690 A).

Also, it has been known that mixed particles composed of non-magnetic iron oxide particles and carbon black particles are used as non-magnetic particles for non-magnetic undercoat layer in order to reduce the surface electrical resistivity value of magnetic recording media (Japanese Patent Application Laid-Open (KOKAI) Nos. 1-213822, 1-300419, 6-236542 and 9-297911 or the like).

#### TECHNICAL PROBLEM TO BE SOLVED BY THE INVENTION

At present, it has been strongly demanded to provide magnetic recording media which exhibit a smooth surface, a smaller light transmittance and a lower surface electrical resistivity value. However, magnetic recording media satisfying all of these properties have not been obtained until now.

Since in the magnetic particles described in Japanese Patent Application Laid-Open (KOKAI) No. 10-269558, carbon black is desorbed or fallen-off from the surfaces thereof, the magnetic recording medium produced by using these magnetic particles is deteriorated in gloss, surface

roughness, linear absorption, friction coefficient and running durability.

It is a technical subject of the present invention to provide magnetic acicular particles for producing a magnetic recording medium exhibiting a smooth surface, a smaller light transmittance, a lower surface electrical resistivity value, and if required, a small friction coefficient and an excellent running durability.

#### MEANS FOR SOLVING THE TECHNICAL PROBLEM

The technical subject described above is accomplished by the present invention as follows.

In an aspect of the present invention, there is provided a magnetic recording medium comprising:

- a non-magnetic base film;

- a non-magnetic undercoat layer formed on said non-magnetic base film; and

- a magnetic recording layer comprising a binder resin and black magnetic acicular composite particles having an average particle diameter of 0.051 to 0.35  $\mu\text{m}$ , comprising as core particles, magnetic acicular cobalt-coated iron oxide particles or magnetic acicular metal particles containing iron as a main component,

- a coating formed on surface of said core particles, comprising organosilane compounds obtainable from alkoxysilane compounds, or polysiloxanes, and

- a carbon black coat formed on said coating layer

comprising said organosilicon compound, in an amount of 0.5 to 10 parts by weight based on 100 parts by weight of said core particles.

In another aspect of the present invention, there is provided a magnetic recording medium comprising:

a non-magnetic base film;

a non-magnetic undercoat layer formed on said non-magnetic base film; and

a magnetic recording layer comprising a binder resin and black magnetic acicular composite particles having an average particle diameter of 0.051 to 0.35  $\mu\text{m}$ , comprising

as core particles, magnetic acicular cobalt-coated iron oxide particles or magnetic acicular metal particles containing iron as a main component,

as a lower layer, a coat formed on the surface of said core particles, comprising at least one compound selected from the group consisting of hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon

a coating formed on the lower layer, comprising organosilane compounds obtainable from alkoxysilane compounds, or polysiloxanes, and

a carbon black adhered on at least a part of said coating in an amount of from more than 10 to 40 parts by weight based on 100 parts by weight of the core particles.

The constitution of the present invention will be explained in more detail.

First, the magnetic recording medium according to the

present invention is described.

The magnetic recording medium according to the present invention comprises a non-magnetic base film; a non-magnetic undercoat layer formed on the non-magnetic base film, which comprises non-magnetic particles and a binder resin; and a magnetic recording layer formed on the non-magnetic undercoat layer, which comprises as magnetic particles, black magnetic acicular composite particles and a binder resin.

The magnetic acicular particles according to the present invention, are composed of black magnetic acicular composite particles comprising as a core particle, magnetic acicular cobalt-coated iron oxide particles or magnetic acicular metal particles containing iron as a main component; a coating layer comprising organosilane compounds obtainable from alkoxysilane compounds or polysiloxanes which is formed on the surface of each core particle, and carbon black coat which are formed on the coating layer comprising the organosilane compounds or polysiloxanes.

As the magnetic acicular cobalt-coated iron oxide particles used in the core particles in the present invention, there may be exemplified magnetic acicular cobalt-coated iron oxide particles obtained by coating with cobalt, both cobalt and iron or the like the surface of acicular magnetite particles ( $\text{FeO}_x \cdot \text{Fe}_2\text{O}_3$ ;  $0 < x < 1$ ), acicular maghemite particles ( $\gamma\text{-Fe}_2\text{O}_3$ ), acicular berthollide compounds particles which are intermediate oxides between maghemite and magnetite.

As the magnetic acicular metal particles containing iron as a main component used in the core particles in the present invention, there may be exemplified magnetic acicular metal iron particles or magnetic acicular metal particles containing iron as a main component which contain elements other than Fe such as Co, Al, Ni, P, Zn, Si, B or rare earth elements.

The core particles used in the present invention have an acicular shape. Meanwhile, the "acicular" used herein means "spindle-shaped", "rice grain-like" or the like in addition to literally "acicular or needle-like".

As to the particle size of the magnetic acicular particles used in the present invention, the average major axial diameter thereof is preferably 0.05 to 0.34  $\mu\text{m}$ , more preferably 0.05 to 0.33  $\mu\text{m}$ , still more preferably 0.05 to 0.32  $\mu\text{m}$ .

When the average major axis diameter of the core particles is more than 0.34  $\mu\text{m}$ , the obtained black magnetic acicular composite particles also may become large particles. In the case where such large particles are used for forming a magnetic recording layer, the surface smoothness of the magnetic recording layer tends to be deteriorated. On the other hand, when the average particle size is less than 0.05  $\mu\text{m}$ , the intermolecular force between the particles may be increased due to the reduction in particle size, so that agglomeration of the particles tends to be caused. Therefore, it becomes difficult to uniformly

coat the surfaces of the core particle with the alkoxysilane compounds or polysiloxanes, and to uniformly form the carbon black coat on the surface of the coating layer comprising the alkoxysilane compounds or polysiloxanes.

The aspect ratio of the magnetic acicular particles as core particles used in the present invention is usually 2.0:1 to 20.0:1, preferably 2.5:1 to 18.0:1, more preferably 3.0:1 to 15.0:1.

When the aspect ratio is more than 20.0:1, the core particles may tend to be entangled with each other, and it also may become difficult to uniformly coat the surfaces of the core particles with the alkoxysilane compounds and to uniformly form the carbon black coat on the surface of the coating layer comprising the alkoxysilane compounds. On the other hand, when the aspect ratio is less than 2.0:1, the strength of the coating film of the magnetic recording medium may be low.

The geometrical standard deviation value of the major axis diameter of the core particles used in the present invention is usually not more than 2.0, preferably not more than 1.8, more preferably not more than 1.6. When the geometrical standard deviation value thereof is more than 2.0, coarse particles may be contained therein, so that the core particles may be inhibited from being uniformly dispersed. Therefore, it may also become difficult to uniformly coat the surfaces of the core particles with the alkoxysilane compounds and to uniformly form the carbon



black coat on the surface of the coating layer comprising the alkoxysilane compounds. The lower limit of the geometrical standard deviation value is 1.01. It is industrially difficult to obtain particles having a geometrical standard deviation value of less than 1.01.

The BET specific surface area of the magnetic acicular particles as core particles used in the present invention is usually 20 to 150 m<sup>2</sup>/g, preferably 25 to 120 m<sup>2</sup>/g, more preferably 28 to 100 m<sup>2</sup>/g. When the BET specific surface area is less than 20 m<sup>2</sup>/g, the core particles may become coarse, or the sintering between the particles may be caused, so that the obtained black magnetic acicular composite particles also may become coarse particles and tend to be deteriorated in smooth surface of the magnetic recording layer. When the BET specific surface area value is more than 150 m<sup>2</sup>/g, the particles may tend to be agglomerated together due to the increase in intermolecular force between the particles because of the fineness thereof, so that it may become difficult to uniformly coat the surfaces of the core particles with the alkoxysilane compounds and to uniformly form the carbon black coat on the surface of the coating layer comprising the alkoxysilane compounds.

The blackness of the core particles used in the present invention, is usually more than 18.0 when represented by L\* value, and the upper limit thereof is usually 34.0, preferably 32.0 when represented by L\* value.

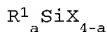
When the  $L^*$  value exceeds 34.0, the lightness of the particles may be high, so that it may be difficult to obtain black magnetic acicular composite particles having a sufficient blackness.

The volume resistivity value of the core particles is usually not less than  $5 \times 10^{10}$   $\Omega \cdot \text{cm}$ .

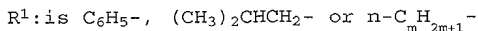
The myristic acid-adsorption of the core particles is usually 0.4 to 1.5.

As to the magnetic properties in case of magnetic acicular cobalt-coated iron oxide particles, the coercive force value thereof is usually 500 to 1700 Oe preferably 550 to 1700 Oe; the saturation magnetization value is usually 60 to 90 emu/g, preferably 65 to 90 emu/g. In case of magnetic acicular metal particles containing iron as a main component, the coercive force value thereof is usually 800 to 3500 Oe, preferably 900 to 3500 Oe; the saturation magnetization value is usually 90 to 170 emu/g, preferably 100 to 170 emu/g.

The organosilane compounds obtainable from alkoxysilane compounds (hereinafter referred to merely as "organosilane compounds"), may be produced by drying or heat-treating alkoxysilane compounds represented by the formula:



wherein



X is  $\text{CH}_3\text{O}-$  or  $\text{C}_2\text{H}_5\text{O}-$ ;

m: an integer of 1 to 18

a: an integer of 0 to 3

Specific examples of the alkoxysilane compounds may include methyltriethoxysilane, dimethyldiethoxysilane, phenyltriethoxysilane, diphenyldiethoxysilane, methyltrimethoxysilane, dimethyldimethoxysilane, phenyltrimethoxysilane, diphenyldimethoxysilane, isobutyltrimethoxysilane, decyltrimethoxysilane or the like.

Among these alkoxysilane compounds, in view of the desorption percentage and the adhering effect of carbon black, methyltriethoxysilane, phenyltriethoxysilane, methyltrimethoxysilane, dimethyldimethoxysilane and isobutyltrimethoxysilane are preferred, and methyltriethoxysilane and methyltrimethoxysilane are more preferred.

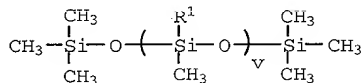
The coating amount of the organosilane compounds is preferably 0.02 to 5.0 % by weight, more preferably 0.03 to 4.0 % by weight, still more preferably 0.05 to 3.0 % by weight (calculated as Si) based on the weight of the core particles coated with the organosilane compounds.

When the coating amount of the organosilane compounds is less than 0.02 % by weight, it becomes difficult to coat the carbon black on the surfaces of the core particles in such an amount enough to improve the blackness, volume resistivity and absorption amount of myristic acid thereof.

On the other hand, when the coating amount of the

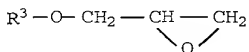
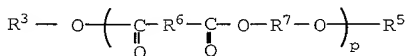
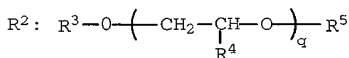
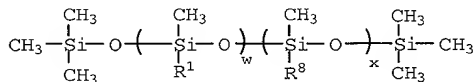
organosilane compounds is more than 5.0 % by weight, it is possible to adhere fully carbon black, but the adhering effect is already saturated and, therefore, the use of such a large coating amount of the organosilane compounds is unnecessary and meaningless.

As the polysiloxanes used in the present invention, there may be exemplified polysiloxanes, modified polysiloxanes and terminal-modified polysiloxanes represented by the formulae:



R<sup>1</sup>: H, CH<sub>3</sub>,

v: 15 to 450



$R^3$ ,  $R^6$  and  $R^7$ :  $-(CH_2)_l-$  and may be the same or different,

$R^4$  and  $R^8$ :  $-(CH_2)_m-CH_3$ ,

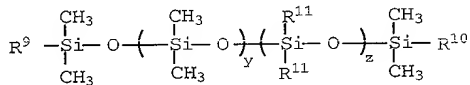
$R^5$ :  $-OH$ ,  $-COOH$ ,  $-CH=CH_2$ ,  $-C=CH_3$  or  $-(CH_2)_n-CH_3$ ,

$l$ : 1 to 15,

$m$ ,  $n$ : 0 to 15,

$w$ : 1 to 50

$x$ : 1 to 300



$R^9$  and  $R^{10}$ :  $-OH$ ,  $R^{12}OH$  or  $R^{13}COOH$  and may be the same or different,

$R^{11}$ :  $-CH_3$  or  $-C_6H_5$ ,

$R^{12}$  and  $R^{13}$ :  $-(CH_2)_p-$ ,

$l$ : 1 to 15,

$y$ : 1 to 200,

$z$ : 0 to 100

In view of the desorption percentage and the adhering effect of carbon black, polysiloxanes having methyl hydrogen siloxane units, the polysiloxanes modified with the polyethers and the polysiloxanes whose terminals are modified with carboxylic acid groups are preferred.

The coating amount of the polysiloxanes is preferably

0.02 to 5.0 % by weight, more preferably 0.03 to 4.0 % by weight, still more preferably 0.05 to 3.0 % by weight (calculated as Si) based on the weight of the core particles coated with the polysiloxanes.

When the coating amount of the polysiloxanes is less than 0.02 % by weight, it becomes difficult to coat the carbon black on the surfaces of the core particles in such an amount enough to improve the blackness, volume resistivity and absorption amount of myristic acid thereof.

On the other hand, when the coating amount of the polysiloxanes is more than 5.0 % by weight, it is possible to adhere fully carbon black, but the adhering effect is already saturated and, therefore, the use of such a large coating amount of the polysiloxanes is unnecessary and meaningless.

The total amount of the carbon black coat is usually 0.5 to 40 parts by weight based on 100 parts by weight of the core particles.

When the amount of the carbon black coat formed is less than 0.5 part by weight, it is difficult to obtain the black magnetic acicular composite particles exhibiting an excellent blackness and volume resistivity.

When the total amount of carbon black coat formed is more than 40 parts by weight, the effects of improving the blackness and the volume resistivity value of the obtained black magnetic acicular composite particles are already saturated and, therefore, the adhesion of such a large

amount of carbon black is unnecessary and meaningless.

When the amount of carbon black coat is large, especially, more than 10 parts by weight, there can be obtained black acicular composite particles exhibiting a well-controlled myristic acid-adsorption. More specifically, such black magnetic acicular composite particles on which carbon black coat is formed in an amount of not more than 10 parts by weight based on 100 parts by weight of the core particles, exhibit a myristic acid-adsorption as high as more than  $0.34 \text{ mg/m}^2$ . On the contrary, the black acicular composite particles on which carbon black coat is formed in an amount of more than 10 parts by weight based on 100 parts by weight of the core particles can exhibit a good myristic acid-adsorption of not more than  $0.3 \text{ mg/m}^2$ .

As the carbon black fine particles used in the present invention, there may be exemplified commercially available carbon blacks such as furnace black, channel black or the like. Specific examples of the commercially available carbon blacks usable in the present invention, may include #3050, #3150, #3250, #3750, #3950, MA100, MA7, #1000, #2400B, #30, MA77, MA8, #650, MA11, #50, #52, #45, #2200B, MA600, etc. (tradename, produced by MITSUBISHI CHEMICAL CORP.), SEAST 9H, SEAST 7H, SEAST 6, SEAST 3H, SEAST 300, SEAST FM, etc. (tradename, produced by TOKAI CARBON CO., LTD.), Raven 1250, Raven 860, Raven 1000, Raven 1190 ULTRA, etc. (tradename, produced by COLOMBIAN CHEMICALS COMPANY),

Ketchen black EC, Ketchen black EC600JD, etc. (tradename, produced by KETCHEN INTERNATIONAL CO., LTD.), BLACK PEARLS-L, BLACK PEARLS 1000, BLACK PEARLS 4630, VULCAN XC72, REGAL 660, REGAL 400, etc. (tradename, produced by CABOTT SPECIALTY CHEMICALS INK CO., LTD.), or the like.

In the consideration of the reducing effect of the myristic acid- adsorption, the carbon black fine particles having a pH value of not more than 9.0 is preferred. Especially, there may be exemplified #3050, #3150, #3250, #3750, #3950, MA100, MA7, #1000, #2400B, #30, MA77, MA8, #650, MA11, #50, #52, #45, #2200B, MA600 (tradename, produced by MITSUBISHI CHEMICAL CORP.), SEAST 9H, SEAST 7H, SEAST 6, SEAST 3H, SEAST 300, SEAST FM (tradename, produced by TOKAI CARBON CO., LTD.), Raven 1250, Raven 860, Raven 1000, Raven 1190 ULTRA (tradename, produced by COLOMBIAN CHEMICALS COMPANY), BLACK PEARLS-L, BLACK PEARLS 1000, BLACK PEARLS 4630, REGAL 660, REGAL 400 (tradename, produced by CABOT SPECIALTY CHEMICALS INK CO., LTD.).

Further, in the consideration of more uniform coat of carbon black to the coating layer comprising at least one organosilicon compound, the carbon black fine particles having a DBP oil absorption of not more than 180 ml/100 g is preferred. Especially, there may be exemplified #3050, #3150, #3250, MA100, MA7, #1000, #2400B, #30, MA77, MA8, #650, MA11, #50, #52, #45, #2200B, MA600 (tradename, produced by MITSUBISHI CHEMICAL CORP.), SEAST 9H, SEAST 7H, SEAST 6, SEAST 3H, SEAST 300, SEAST FM (tradename, produced



by TOKAI CARBON CO., LTD.), Raven 1250, Raven 860, Raven 1000, Raven 1190 ULTRA (tradename, produced by COLOMBIAN CHEMICALS COMPANY), BLACK PEARLS-L, BLACK PEARLS 1000, BLACK PEARLS 4630, REGAL 660, REGAL 400 (tradename, produced by CABOT SPECIALTY CHEMICALS INK CO., LTD.).

The average particle size of the carbon black fine particles used is preferably 0.002 to 0.05  $\mu\text{m}$ , more preferably 0.005 to 0.035  $\mu\text{m}$ .

When the average particle size of the carbon black fine particles used is less than 0.002  $\mu\text{m}$ , the carbon black fine particles used are too fine to be well handled.

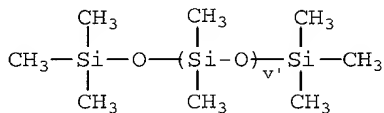
On the other hand, when the average particle size of the carbon black fine particles used is more than 0.05  $\mu\text{m}$ , since the carbon black fine particles used is much larger, it is necessary to apply a larger mechanical shear force for forming the uniform carbon black coat on the coating layer composed of the alkoxysilane compounds or the polysiloxanes, thereby rendering the coating process industrially disadvantageous.

In the present invention, when the amount of carbon black coat is large, especially more than 10 parts by weight based on 100 parts by weight of the core particles, at least two carbon black coats bonded together are formed onto the coating of organosilane compounds obtainable from alkoxysilane compounds or polysiloxanes.

In the consideration of the desorption percentage and adhering effect of carbon black, the amount of the carbon

black coat (hereinafter referred to merely as "first carbon black coat") formed onto the coating of the organosilane compounds obtainable from the alkoxysilane compounds or the polysiloxanes is usually 0.5 to 10 parts by weight, preferably preferably 3 to 10 parts by weight based on 100 parts by weight of the core particles; and the amount of the carbon black coat (hereinafter referred to merely as "second carbon black coat") formed onto the surface of the first carbon black coat through adhesives is usually 1 to 30 parts by weight, preferably 5 to 25 parts by weight based on 100 parts by weight of the core particles.

In the present invention, the first and second carbon black coats may be integrated together by bonding carbon black of the respective coats with each other using an adhesive. In order to firmly and uniformly bond the carbon black coats with each other and control the myristic acid-adsorption to an appropriate level, it is preferred to use as the adhesive, dimethyl polysiloxane represented by the following formula:



wherein  $v'$  is a is an integer of 15 to 450.

The amount of the adhesive used is 0.1 to 5 parts by weight based on 100 parts by weight of the core particles.

When the amount of the adhesive used is less than 0.1 part by weight, it may be difficult to sufficiently bond the second carbon black coat onto the first carbon black coat. As a result, it may be difficult to improve the myristic acid-adsorption of the obtained black magnetic acicular composite particles.

When the amount of the adhesive used is more than 5 parts by weight, although the carbon black coats can be sufficiently bonded together, the effect is already saturated and, therefore, the use of such a large amount of the adhesive is unnecessary and meaningless.

The particle shape and size of the black magnetic acicular composite particles according to the present invention, are considerably varied depending upon those of the core particles. More specifically, the particle shape or configuration of the magnetic acicular composite particles is similar to that of the core particles, and the particle size of the magnetic acicular composite particles is slightly larger than that of the core particles.

That is, the black magnetic acicular composite particles according to the present invention, have an average major axial diameter of usually 0.051 to 0.35  $\mu\text{m}$ , preferably 0.051 to 0.34  $\mu\text{m}$ , more preferably 0.051 to 0.33  $\mu\text{m}$ ; and an aspect ratio of usually 2.0:1 to 20.0:1, preferably 2.5:1 to 18.0:1, more preferably 3.0:1 to 15.0:1.

When the average major axial diameter is more than 0.35  $\mu\text{m}$ , the obtained black magnetic acicular composite

particles become too large. In the case where such large particles are used, the obtained magnetic recording layer may tend to be deteriorated in surface smoothness of coating film. When the average major axial diameter is less than  $0.051\text{ }\mu\text{m}$ , the intermolecular force between the particles may become too large due to fineness thereof, so that the obtained composite particles may tend to be agglomerated together, resulting in deteriorated dispersibility in vehicle upon the production of a magnetic coating composition.

When the aspect ratio is more than 20.0:1, the particles may tend to be entangled or interlaced with each other, sometimes resulting in deteriorated dispersibility in vehicle upon the production of a magnetic coating composition and increased viscosity of the magnetic coating composition. When the aspect ratio is less than 2.0:1, the strength of coating film of the obtained magnetic recording medium using such particles may become small.

The geometrical standard deviation value of major axial diameters of the black magnetic acicular composite particles according to the present invention is usually not more than 2.0. When the geometrical standard deviation value is more than 2.0, coarse particles may be present in the obtained magnetic acicular composite particles, thereby adversely affecting the surface smoothness of the obtained coating film. In the consideration of the surface smoothness of coating film, the geometrical standard

deviation value is preferably not more than 1.8, more preferably not more than 1.6. In the consideration of industrial productivity, the geometrical standard deviation value is not less than 1.01. Meanwhile, the particles having a geometrical standard deviation value of less than 1.01 are difficult to industrially produce.

The black magnetic acicular composite particles of the present invention, have a myristic acid absorption of usually 0.01 to 0.3 mg/m<sup>2</sup>, preferably 0.01 to 0.29 mg/m<sup>2</sup>, more preferably 0.01 to 0.28 mg/m<sup>2</sup>.

When the myristic acid-adsorption of the black magnetic acicular composite particles is within the above-specified range, the amount of myristic acid absorbed thereinto is adequate, so that the amount of myristic acid oozed onto the surface of the magnetic recording layer can be readily controlled to an appropriate level. As a result, upon the repeated use of magnetic tape, it is possible to maintain a sufficiently low friction coefficient of the magnetic tape for a long period of time, thereby ensuring an excellent running property thereof.

The black magnetic acicular composite particles according to the present invention have a BET specific surface area of preferably 21 to 160 m<sup>2</sup>/g, more preferably 26 to 130 m<sup>2</sup>/g, still more preferably 29 to 110 m<sup>2</sup>/g. When the BET specific surface area is less than 21 m<sup>2</sup>/g, the obtained black magnetic acicular composite particles may tend to become coarse or be sintered together. In the case

where such particles are used to produce a magnetic recording layer, the obtained coating film may tend to be deteriorated in surface smoothness. When the BET specific surface area is more than  $160 \text{ m}^2/\text{g}$ , the intermolecular force between the particles may be increased due to fineness thereof. As a result, the obtained particles may tend to be agglomerated together, resulting in deteriorated dispersibility in vehicle upon the production of magnetic coating composition.

As to the blackness of the black magnetic acicular composite particles, the  $L^*$  value thereof is usually not more than 23, preferably not more than 22, more preferably not more than 21. When the  $L^*$  value is more than 23, the lightness of the particles becomes too high, thereby failing to obtain particles having a sufficient blackness. The  $L^*$  value of the black magnetic acicular composite particles thereof is not less than 15.

The black magnetic acicular composite particles have a volume resistivity value of preferably not more than  $1.0 \times 10^7 \text{ } \Omega \cdot \text{cm}$ , more preferably  $1.0 \times 10^3$  to  $5.0 \times 10^6 \text{ } \Omega \cdot \text{cm}$ , still more preferably  $1.0 \times 10^3$  to  $1.0 \times 10^6 \text{ } \Omega \cdot \text{cm}$ . When the volume resistivity value is more than  $1.0 \times 10^7 \text{ } \Omega \cdot \text{cm}$ , it is difficult to sufficiently reduce the surface electrical resistivity value of the obtained magnetic recording medium.

The carbon black desorption percentage of the black magnetic acicular composite particles is preferably not more than 20%, more preferably not more than 10%. When the

carbon black desorption percentage is more than 20%, the obtained particles may tend to be inhibited from uniformly dispersed in vehicle due to desorbed and liberated carbon black upon the production of magnetic recording media.

As to magnetic properties of the black magnetic acicular composite particles according to the present invention, in the case where the magnetic acicular cobalt-coated iron oxide particles are used as the core particles, the coercive force value thereof is preferably 500 to 1,700 Oe, more preferably 550 to 1,700 Oe; and the saturation magnetization value thereof is preferably 60 to 90 emu/g, more preferably 65 to 90 emu/g. In the case where the magnetic acicular metal particles containing iron as a main component are used as the core particles, the coercive force value thereof is preferably 800 to 3,500 Oe, more preferably 900 to 3,500 Oe; and the saturation magnetization value thereof is preferably 90 to 170 emu/g, more preferably 100 to 170 emu/g.

The thickness of carbon black coat is preferably not more than 0.04  $\mu\text{m}$ , more preferably not more than 0.02  $\mu\text{m}$ , still more preferably not more than 0.01  $\mu\text{m}$ .

The surface of the core particle used in the present invention may be coated with at least one selected from the group consisting of a hydroxide of aluminum, an oxide of aluminum, a hydroxide of silicon and an oxide of silicon (hereinafter referred to as "hydroxides of aluminum or the like"). When the black magnetic acicular composite

particles obtained by using as core particles which are coated with the hydroxides of aluminum or the like, are dispersed in a vehicle, since it is possible to more effectively reduce the carbon black desorption percentage, it is more easy to obtain a desired dispersibility.

The amount of the hydroxides of aluminum or the like coat is usually not more than 20 % by weight, preferably 0.01 to 20 % by weight (calculated as Al and/or  $\text{SiO}_2$ ) based on the total weight of the core particles coated.

If it is less than 0.01 % by weight (calculated as Al and/or  $\text{SiO}_2$ ) based on the total weight of the core particles coated, the dispersibility-improving effect by coating therewith may be insufficient.

When the coating amount of the hydroxide of aluminum or the like is more than 20% by weight, although there can be obtained a sufficient effect of reducing the percentage of carbon black desorbed or fallen-off from the surfaces of the core particles, the effect is already saturated and, therefore, the use of such a large coating amount of the hydroxide of aluminum or the like is unnecessary and meaningless.

The particle size, geometrical standard deviation value, BET specific surface area, blackness  $L^*$  value, volume resistivity and magnetic properties of the black magnetic acicular composite particles wherein the surface of the core particle is coated with the hydroxide of aluminum or the like according to the present invention, are substantially



particles obtained by using as core particles which are coated with the hydroxides of aluminum or the like, are dispersed in a vehicle, since it is possible to more effectively reduce the carbon black desorption percentage, it is more easy to obtain a desired dispersibility.

The amount of the hydroxides of aluminum or the like coat is usually not more than 20 % by weight, preferably 0.01 to 20 % by weight (calculated as Al and/or  $\text{SiO}_2$ ) based on the total weight of the core particles coated.

If it is less than 0.01 % by weight (calculated as Al and/or  $\text{SiO}_2$ ) based on the total weight of the core particles coated, the dispersibility-improving effect by coating therewith may be insufficient.

When the coating amount of the hydroxide of aluminum or the like is more than 20% by weight, although there can be obtained a sufficient effect of reducing the percentage of carbon black desorbed or fallen-off from the surfaces of the core particles, the effect is already saturated and, therefore, the use of such a large coating amount of the hydroxide of aluminum or the like is unnecessary and meaningless.

The particle size, geometrical standard deviation value, BET specific surface area, blackness  $L^*$  value, volume resistivity and magnetic properties of the black magnetic acicular composite particles wherein the surface of the core particle is coated with the hydroxide of aluminum or the like according to the present invention, are substantially

the same as those of the black magnetic acicular composite particles wherein the core particle is uncoated with the hydroxide of aluminum or the like according to the present invention.

In addition, the desorption percentage of carbon black of the black magnetic acicular composite particles wherein the surface of the core particle is coated with the hydroxide of aluminum or the like is more improved as compared with that of the black magnetic acicular composite particles wherein the core particle is uncoated therewith. The carbon black desorption percentage of the black magnetic acicular composite particles wherein the surface of the core particle is coated with the hydroxide of aluminum or the like, is preferably not more than 10 %, more preferably not more than 5 %.

As the non-magnetic base film, the following materials which are at present generally used for the production of a magnetic recording medium are usable as a raw material: a synthetic resin such as polyethylene terephthalate, polyethylene, polypropylene, polycarbonate, polyethylene naphthalate, polyamide, polyamideimide and polyimide; foil and plate of a metal such as aluminum and stainless steel; and various kinds of paper. The thickness of the non-magnetic base film varies depending upon the material, but it is usually about 1.0 to 300  $\mu\text{m}$ , preferably 2.0 to 200  $\mu\text{m}$ .

In the case of a magnetic disc, polyethylene terephthalate is usually used as the non-magnetic base film,

and the thickness thereof is usually 50 to 300  $\mu\text{m}$ , preferably 60 to 200  $\mu\text{m}$ . In a magnetic tape, when polyethylene terephthalate is used as the non-magnetic base film, the thickness thereof is usually 3 to 100  $\mu\text{m}$ , preferably 4 to 20  $\mu\text{m}$ ; when polyethylene naphthalate is used, the thickness thereof is usually 3 to 50  $\mu\text{m}$ , preferably 4 to 20  $\mu\text{m}$ ; and when polyamide is used, the thickness thereof is usually 2 to 10  $\mu\text{m}$ , preferably 3 to 7  $\mu\text{m}$ .

As the binder resin used in the present invention, the following resins which are at present generally used for the production of a magnetic recording medium are usable: vinyl chloride-vinyl acetate copolymer, polyurethane resin, vinyl chloride-vinyl acetate-maleic acid copolymer, urethane elastomer, butadiene-acrylonitrile copolymer, polyvinyl butyral, cellulose derivative such as nitrocellulose, polyester resin, synthetic rubber resin such as polybutadiene, epoxy resin, polyamide resin, polyisocyanate, electron radiation curing acryl urethane resin and mixtures thereof.

Each of these resin binders may contain a functional group such as  $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{SO}_3\text{M}$ ,  $-\text{OPO}_2\text{M}_2$  and  $-\text{NH}_2$ , wherein M represents H, Na or K. With the consideration of the dispersibility of the black magnetic acicular composite particles, a binder resin containing a functional group  $-\text{COOH}$  or  $-\text{SO}_3\text{M}$  is preferable.

The thickness of the magnetic recording layer obtained

by applying the magnetic coating composition on the surface of the non-magnetic base film and dried, is usually in the range of 0.01 to 5.0  $\mu\text{m}$ . If the thickness is less than 0.01  $\mu\text{m}$ , uniform coating may be difficult, so that unfavorable phenomenon such as unevenness on the coating surface is observed. On the other hand, when the thickness exceeds 5.0  $\mu\text{m}$ , it may be difficult to obtain desired signal recording property due to an influence of diamagnetism. The preferable thickness is in the range of 0.1 to 4.0  $\mu\text{m}$ .

The mixing ratio of the black magnetic acicular composite particles with the binder resin is usually 5 to 2000 parts by weight, preferably 100 to 1000 parts by weight based on 100 parts by weight of the binder resin.

When the amount of the black magnetic acicular composite particles blended is less than 5 parts by weight, the obtained magnetic coating composition contains a too small amount of the black magnetic acicular composite particles. As a result, when a coating film is produced from such a magnetic coating composition, it is not possible to obtain a coating film in which the black magnetic acicular composite particles are continuously dispersed, so that the surface smoothness and the strength of the coating film become unsatisfactory. On the other hand, when the amount of the black magnetic acicular composite particles blended is more than 2,000 parts by weight, the amount of the black magnetic acicular composite particles becomes too large relative to that of the binder resin, so that it is not

possible to sufficiently disperse the black magnetic acicular composite particles in the magnetic coating composition. As a result, when a coating film is produced from such a magnetic coating composition, it is difficult to obtain a coating film having a sufficiently smooth surface. Further, since the black magnetic acicular composite particles cannot be sufficiently bound with each other by the binder resin, the obtained coating film tends to become brittle.

In the magnetic recording medium according to the present invention, the amount of carbon black fine particles added to the magnetic recording layer thereof can be reduced to usually less than 6 parts by weight, preferably less than 5 parts by weight, more preferably less than 3 parts by weight based on 100 parts by weight of the black magnetic acicular composite particles.

Further, in the case where the black magnetic acicular composite particles having a large particle size are used as magnetic particles, it can be expected to omit the addition of the carbon black fine particles to the magnetic recording layer.

Incidentally, the magnetic recording layer may optionally contain a lubricant, an abrasive, an anti-static agent and other additives which are usually used for the production of magnetic recording media, in an amount of 0.1 to 50 parts by weight based on 100 parts of the binder resin.

The thickness of the non-magnetic undercoat layer is preferably 0.2 to 10.0  $\mu\text{m}$ . When the thickness of the non-magnetic undercoat layer is less than 0.2  $\mu\text{m}$ , it may be difficult to improve the surface roughness of the non-magnetic substrate, and the stiffness of a coating film formed thereon tends to be unsatisfactory. In the consideration of reduction in total thickness of the magnetic recording medium as well as the stiffness of the coating film, the thickness of the non-magnetic undercoat layer is more preferably in the range of 0.5 to 5.0  $\mu\text{m}$ .

As the binder resin, the same binder resin as that used for the production of the magnetic recording layer is usable.

The mixing ratio of the non-magnetic particles to the binder resin is usually 5 to 2000 parts by weight, preferably 100 to 1000 parts by weight based on 100 parts by weight of the binder resin.

When the content of the non-magnetic particles is as small as less than 5 parts by weight, such a non-magnetic undercoat layer in which the non-magnetic particles are uniformly and continuously dispersed may not be obtained upon coating, resulting in insufficient surface smoothness and insufficient stiffness of the non-magnetic substrate. When the content of the non-magnetic particles is more than 2,000 parts by weight, the non-magnetic particles may not be sufficiently dispersed in a non-magnetic coating composition since the amount of the non-magnetic particles is too large

as compared to that of the binder resin. As a result, when such a non-magnetic coating composition is coated onto the non-magnetic base film, it may become difficult to obtain a coating film having a sufficiently smooth surface. Further, since the non-magnetic particles may not be sufficiently bonded together through the binder resin, the obtained coating film tends to become brittle.

It is possible to add an additive such as a lubricant, a polishing agent, an antistatic agent, etc. which are generally used for the production of a magnetic recording medium, to the non-magnetic undercoating layer. The mixing ratio of the additive to the binder resin is preferably 0.1 to 50 parts by weight based on 100 parts by weight of the binder resin.

As the non-magnetic particles used in the non-magnetic undercoat layer of the present invention, there may be exemplified non-magnetic inorganic particles ordinarily used for forming a non-magnetic undercoat layer in conventional magnetic recording media. Specific examples of the non-magnetic particles may include hematite particles, iron oxide hydroxide particles, titanium oxide particles, zinc oxide particles, tin oxide particles, tungsten oxide particles, silicon dioxide particles,  $\alpha$ -alumina particles,  $\beta$ -alumina particles,  $\gamma$ -alumina particles, chromium oxide particles, cerium oxide particles, silicon carbide particles, titanium carbide particles, silicon nitride particles, boron nitride particles, calcium carbonate

particles, barium carbonate particles, magnesium carbonate particles, strontium carbonate particles, calcium sulfate particles, barium sulfate particles, molybdenum disulfide particles, barium titanate particles or the like. These non-magnetic particles may be used singly or in the form of a mixture of any two or more thereof. Among them, the use of hematite particles, iron oxide hydroxide particles, titanium oxide particles and the like is preferred.

In the present invention, in order to improve the dispersibility of the non-magnetic particles in vehicle upon the production of non-magnetic coating composition, the non-magnetic particles may be surface-treated with hydroxides of aluminum, oxides of aluminum, hydroxides of silicon, oxides of silicon or the like to form a coat made of any of these compounds on the surfaces thereof. Further, the non-magnetic particles may contain Al, Ti, Zr, Mn, Sn, Sb or the like inside thereof, if required, in order to improve various properties of the obtained magnetic recording media such as light transmittance, surface electrical resistivity, mechanical strength, surface smoothness, durability or the like.

The particle shape of the non-magnetic particles may include a granular shape such as a spherical shape, an irregular (anisotropic) shape, an octahedral shape, a hexahedral shape, a polyhedral shape or the like; an acicular shape such as a needle shape, a spindle shape, a rice ball shape or the like; and a plate shape, or the like.



As the average particle size of the non-magnetic particles, the average major axis diameter is usually 0.01 to 0.3  $\mu\text{m}$ , preferably 0.015 to 0.25  $\mu\text{m}$ , more preferably 0.02 to 0.2  $\mu\text{m}$ .

In case of using the black magnetic acicular composite particles, wherein the magnetic acicular cobalt-coated iron oxide particles are used as core particles, which are coated with no hydroxides of aluminum or the like, the magnetic recording medium of the present invention has a coercive force of usually 500 to 1,700 Oe, preferably 550 to 1,700 Oe; a squareness (residual magnetic flux density  $B_r$ /saturation magnetic flux density  $B_m$ ) of usually 0.85 to 0.95, preferably 0.86 to 0.95; a gloss (of the coating film) of usually 165 to 300 %, preferably 170 to 300 %; a surface roughness  $R_a$  (of the coating film) of usually not more than 11.0 nm, preferably 2.0 to 10.5 nm, more preferably 2.0 to 10.0 nm, a Young's modulus of usually 125 to 160, preferably 126 to 160; a linear adsorption coefficient (of the coating film) of usually 1.40 to 10.0  $\mu\text{m}^{-1}$ , preferably 1.45 to 10.0  $\mu\text{m}^{-1}$ ; and a surface electrical resistivity of usually not more than  $1.0 \times 10^9 \Omega/\text{cm}^2$ , preferably not more than  $7.5 \times 10^8 \Omega/\text{cm}^2$ , more preferably not more than  $5.0 \times 10^8 \Omega/\text{cm}^2$ ; a running durability time thereof of usually not less than 25 minutes, preferably not less than 26 minutes.

In case of using the black magnetic acicular composite particles wherein a large amount of carbon black is adhered and the magnetic acicular cobalt-coated iron oxide particles

which are coated with no hydroxides of aluminum or the like, the magnetic recording medium not only can satisfy the above described properties, but also can exhibit a linear absorption (of coating film) of usually  $1.80$  to  $10.00 \mu\text{m}^{-1}$ , preferably  $1.85$  to  $10.00 \mu\text{m}^{-1}$ ; a surface electrical resistivity value (of coating film) of usually not more than  $1.0 \times 10^8 \Omega/\text{cm}^2$ , preferably not more than  $7.5 \times 10^7 \Omega/\text{cm}^2$ , more preferably not more than  $5.0 \times 10^7 \Omega/\text{cm}^2$ ; a friction coefficient of usually  $0.25$  to  $0.30$ , preferably  $0.25$  to  $0.29$ ; and a running durability time thereof of usually not less than  $26$  minutes, preferably not less than  $27$  minutes.

In case of using the black magnetic acicular composite particles, wherein the magnetic acicular metal particles containing iron as a main component are used as core particles which are coated with no hydroxides of aluminum or the like, the magnetic recording medium of the present invention has a coercive force of usually  $800$  to  $3,500$  Oe, preferably  $900$  to  $3,500$  Oe; a squareness (residual magnetic flux density  $B_r$ /saturation magnetic flux density  $B_m$ ) of usually  $0.85$  to  $0.95$ , preferably  $0.86$  to  $0.95$ ; a gloss (of the coating film) of usually  $185$  to  $300 \%$ , preferably  $195$  to  $300 \%$ ; a surface roughness  $R_a$  (of the coating film) of usually not more than  $11.0 \text{ nm}$ , preferably  $2.0$  to  $10.5 \text{ nm}$ , more preferably  $2.0$  to  $10.0 \text{ nm}$ , a Young's modulus of usually  $125$  to  $160$ , preferably  $126$  to  $160$ ; a linear adsorption coefficient (of the coating film) of usually  $1.40$  to  $10.0 \mu\text{m}^{-1}$ , preferably  $1.45$  to  $10.0 \mu\text{m}^{-1}$ ; and a surface electrical

resistivity of usually not more than  $1.0 \times 10^9 \Omega/\text{cm}^2$ , preferably not more than  $7.5 \times 10^8 \Omega/\text{cm}^2$ , more preferably not more than  $5.0 \times 10^8 \Omega/\text{cm}^2$ ; a running durability time thereof of usually not less than 25 minutes, preferably not less than 26 minutes.

In case of using the black magnetic acicular composite particles wherein a large amount of carbon black is adhered and the magnetic acicular metal particles containing iron as a main component which are coated with no hydroxides of aluminum or the like, the magnetic recording medium not only can satisfy the above described properties, but also can exhibit a linear absorption (of coating film) of usually  $1.80$  to  $10.00 \mu\text{m}^{-1}$ , preferably  $1.85$  to  $10.00 \mu\text{m}^{-1}$ ; a surface electrical resistivity value (of coating film) of usually not more than  $1.0 \times 10^8 \Omega/\text{cm}^2$ , preferably not more than  $7.5 \times 10^7 \Omega/\text{cm}^2$ , more preferably not more than  $5.0 \times 10^7 \Omega/\text{cm}^2$ ; a friction coefficient of usually  $0.25$  to  $0.30$ , preferably  $0.25$  to  $0.29$ ; and a running durability time thereof of usually not less than 26 minutes, preferably not less than 27 minutes.

In case of using the black magnetic acicular composite particles, wherein the magnetic acicular cobalt-coated iron oxide particles as core particles which are coated with hydroxides of aluminum or the like, the magnetic recording medium of the present invention has a coercive force of usually  $500$  to  $1,700 \text{ Oe}$ , preferably  $550$  to  $1,700 \text{ Oe}$ ; a

squareness (residual magnetic flux density  $B_r$ /saturation magnetic flux density  $B_m$ ) of usually 0.85 to 0.95, preferably 0.86 to 0.95; a gloss (of the coating film) of usually 170 to 300 %, preferably 175 to 300 %; a surface roughness  $R_a$  (of the coating film) of usually not more than 10.0 nm, preferably 2.0 to 9.5 nm, more preferably 2.0 to 9.0 nm, a Young's modulus of usually 127 to 160, preferably 128 to 160; a linear adsorption coefficient (of the coating film) of usually  $1.45$  to  $10.0 \mu\text{m}^{-1}$ , preferably  $1.50$  to  $10.0 \mu\text{m}^{-1}$ ; and a surface electrical resistivity of usually not more than  $1.0 \times 10^9 \Omega/\text{cm}^2$ , preferably not more than  $7.5 \times 10^8 \Omega/\text{cm}^2$ , more preferably not more than  $5.0 \times 10^8 \Omega/\text{cm}^2$ ; a running durability time thereof of usually not less than 27 minutes, preferably not less than 28 minutes.

In case of using the black magnetic acicular composite particles wherein a large amount of carbon black is adhered and the magnetic acicular cobalt-coated iron oxide particles which are coated with hydroxides of aluminum or the like, the magnetic recording medium not only can satisfy the above described properties, but also can exhibit a linear absorption (of coating film) of usually  $1.85$  to  $10.00 \mu\text{m}^{-1}$ , preferably  $1.90$  to  $10.00 \mu\text{m}^{-1}$ ; a surface electrical resistivity value (of coating film) of usually not more than  $5.0 \times 10^7 \Omega/\text{cm}^2$ , preferably not more than  $2.5 \times 10^7 \Omega/\text{cm}^2$ , more preferably not more than  $1.0 \times 10^7 \Omega/\text{cm}^2$ ; a friction coefficient of usually 0.21 to 0.26, preferably 0.21 to

0.25; and a running durability time thereof of usually not less than 27 minutes, preferably not less than 28 minutes.

In case of using the black magnetic acicular composite particles, wherein the magnetic acicular metal particles containing iron as a main component as core particles which are coated with hydroxides of aluminum or the like, the magnetic recording medium of the present invention has a coercive force of usually 800 to 3500 Oe, preferably 900 to 3500 Oe; a squareness (residual magnetic flux density  $B_r$ /saturation magnetic flux density  $B_m$ ) of usually 0.85 to 0.95, preferably 0.86 to 0.95; a gloss (of the coating film) of usually 190 to 300 %, preferably 200 to 300 %; a surface roughness  $R_a$  (of the coating film) of usually not more than 10.0 nm, preferably 2.0 to 9.5 nm, more preferably 2.0 to 9.0 nm, a Young's modulus of usually 127 to 160, preferably 128 to 160; a linear adsorption coefficient (of the coating film) of usually  $1.45$  to  $10.0 \mu\text{m}^{-1}$ , preferably  $1.50$  to  $10.0 \mu\text{m}^{-1}$ ; and a surface electrical resistivity of usually not more than  $1.0 \times 10^9 \Omega/\text{cm}^2$ , preferably not more than  $7.5 \times 10^8 \Omega/\text{cm}^2$ , more preferably not more than  $5.0 \times 10^8 \Omega/\text{cm}^2$ ; a running durability time thereof of usually not less than 27 minutes, preferably not less than 28 minutes.

In case of using the black magnetic acicular composite particles wherein a large amount of carbon black is adhered and the magnetic acicular metal particles containing iron as a main component which are coated with no hydroxides of aluminum or the like, the magnetic recording medium not only

can satisfy the above described properties, but also can exhibit a linear absorption (of coating film) of usually 1.85 to 10.00  $\mu\text{m}^{-1}$ , preferably 1.90 to 10.00  $\mu\text{m}^{-1}$ ; a surface electrical resistivity value (of coating film) of usually not more than  $5.0 \times 10^7 \Omega/\text{cm}^2$ , preferably not more than  $2.5 \times 10^7 \Omega/\text{cm}^2$ , more preferably not more than  $1.0 \times 10^7 \Omega/\text{cm}^2$ ; a friction coefficient of usually 0.21 to 0.26, preferably 0.21 to 0.25; and a running durability time thereof of usually not less than 27 minutes, preferably not less than 28 minutes.

The black magnetic acicular composite particles according to the present invention can be produced by the following method.

As the core particles used in the present invention, known Co-coated magnetic acicular iron oxide particles and magnetic acicular metal particles containing iron as a main component may be used.

The coating of the core particles with the alkoxysilane compounds or the polysiloxanes, may be conducted by mechanically mixing and stirring the core particles together with the alkoxysilane compounds or the polysiloxanes; or by mechanically mixing and stirring both the components together while spraying the alkoxysilane compounds or the polysiloxanes onto the core particles. In these cases, substantially whole amount of the alkoxysilane compounds or the polysiloxanes added can be applied onto the surfaces of the core particles.

In order to uniformly coat the surfaces of the core particles with the alkoxysilane compounds or the polysiloxanes, it is preferred that the core particles are preliminarily diagggregated by using a pulverizer.

As apparatus for mixing and stirring treatment of the core particles with the alkoxysilane compounds or the polysiloxanes to form the coating layer thereof, and as apparatus for mixing and stirring treatment of carbon black fine particles with the particles whose surfaces are coated with the alkoxysilane compounds or the polysiloxanes to form the carbon black coat, there may be preferably used those apparatus capable of applying a shear force to the particles, more preferably those apparatuses capable of conducting the application of shear force, spatulate force and compressed force at the same time. As such apparatuses, there may be exemplified wheel-type kneaders, ball-type kneaders, blade-type kneaders, roll-type kneaders or the like.

Specific examples of the wheel-type kneaders may include a mix muller, a Simpson mill or a sand mill, a multi-mull, a Stotz mill, a wet pan mill, a Conner mill, a Henschel mixer, a ring muller, a revolving mill, a vibrating mill, a pressure kneader, an extruder, a screw mixer or the like. Among them, a mix muller, a Simpson mill, a sand mill, a multi-mull, a Stotz mill, a wet pan mill, a Conner mill and Henschel mixer are more preferred. Especially, a mix muller, a Simpson mill, a sand mill and a multi-mull are

more preferred.

In order to coat the surfaces of the core particles with the alkoxyasilane compounds or the polysiloxanes as uniformly as possible, the conditions of the above mixing or stirring treatment may be appropriately controlled such that the linear load is usually 2 to 200 Kg/cm, preferably 10 to 150 Kg/cm, more preferably 15 to 100 Kg/cm; and the treating time is usually 5 to 120 minutes, preferably 10 to 90 minutes. It is preferred to appropriately adjust the stirring speed in the range of usually 2 to 2,000 rpm, preferably 5 to 1,000 rpm, more preferably 10 to 800 rpm.

The amount of the alkoxyasilane compounds or the polysiloxanes added, is preferably 0.15 to 45 parts by weight based on 100 parts by weight of the magnetic acicular particles. When the amount of the alkoxyasilane compounds or the polysiloxanes added, is less than 0.15 parts by weight, it becomes difficult to adhere enough amount of the carbon black so as to improve a blackness and lower a volume resistivity. When the amount of the alkoxyasilane compounds or the polysiloxanes added, is more than 45 parts by weight, it is possible to adhere a large amount of carbon black, but the use of such a large amount thereof is unnecessary and meaningless.

After coating the surfaces of the core particles with the alkoxyasilane compounds or the polysiloxanes, adding the carbon black fine particles to the core particles coated with the alkoxyasilane compounds or the polysiloxanes, and



adhering carbon black onto the core particles, the obtained black magnetic acicular composite particles may be dried or heat-treated.

It is preferred that the carbon black fine particles are added little by little and slowly, especially about 5 to 60 minutes.

In order to form carbon black coat onto the coating layer composed of the alkoxysilane compounds or the polysiloxanes as uniformly as possible, the conditions of the above mixing or stirring treatment can be appropriately controlled such that the linear load is usually 2 to 200 Kg/cm, preferably 10 to 150 Kg/cm, more preferably 15 to 100 Kg/cm; and the treating time is usually 5 to 120 minutes, preferably 10 to 90 minutes. It is preferred to appropriately adjust the stirring speed in the range of usually 2 to 2,000 rpm, preferably 5 to 1,000 rpm, more preferably 10 to 800 rpm.

The amount of carbon black fine particles added is 0.5 to 40 parts by weight based on 100 parts by weight of the core particles. When the amount of carbon black fine particles added is less than 0.5 part by weight, the amount of carbon black coat may become too small. As a result, it may be difficult to obtain black magnetic acicular composite particles having an excellent blackness and a low volume resistivity value. When the amount of carbon black fine particles added is more than 40 parts by weight, the effect of improving the blackness and the volume resistivity value

of the obtained black magnetic acicular composite particles is already saturated and, therefore, the addition of such a large amount of carbon black fine particles is unnecessary and meaningless.

In particular, in order to obtain black magnetic acicular composite particles having a carbon black coat in a large amount, it is preferred to add carbon black in two or more separate parts while alternately repeating the addition and adhesion thereof. Especially, when carbon black fine particles for forming the second carbon black coat is added and adhered onto the first carbon black coat, it is preferred to adhere an adhesive onto the first carbon black coat prior to the addition of carbon black fine particles for the second carbon black coat.

More specifically, the adhesive is added to the composite particles on which the first carbon black coat is formed, and the resultant mixture is mixed and stirred together to adhere the adhesive onto the particles. Then, carbon black fine particles are further added to the obtained composite particles, and these particles are mixed and stirred together to form the carbon black coat onto the first carbon black coat, thereby forming the second carbon black coat on the first carbon black coat.

The mixing and stirring conditions with the adhesives may be adequately controlled such that the linear load is usually 2 to 200 Kg/cm, preferably 10 to 150 Kg/cm, more preferably 15 to 100 Kg/cm; the treating time is usually 5

to 120 minutes, preferably 10 to 90 minutes; and the stirring speed is usually 2 to 2,000 rpm, preferably 5 to 1,000 rpm, more preferably 10 to 800 rpm.

The amount of the adhesive added is 0.1 to 5 parts by weight based on 100 parts by weight of the core particles. When the amount of the adhesive added is less than 0.1 part by weight, it may become difficult to form a sufficient amount of carbon black coat on the first carbon coat, thereby failing to form a sufficient second carbon black coat thereon. When the amount of the adhesive added is more than 5 parts by weight, the adhesion effect is already saturated and, therefore, it is unnecessary and meaningless to add such a large amount of the adhesive.

The mixing and stirring conditions upon adhesion of the second carbon black coat may be appropriately selected such that the carbon black can be uniformly adhered to the adhesive. More specifically, the treating conditions may be adequately controlled such that the linear load is usually 2 to 200 Kg/cm, preferably 10 to 150 Kg/cm, more preferably 15 to 100 Kg/cm; the treating time is 5 to 120 minutes, preferably 10 to 90 minutes; and the stirring speed is usually 2 to 2,000 rpm, preferably 5 to 1,000 rpm, more preferable 10 to 800 rpm.

The amount of carbon black fine particles added for forming the second carbon black coat is 1 to 30 parts by weight based on 100 parts by weight of the core particles. When the amount of the carbon black fine particles added is

less than 1 part by weight, the amount of carbon black adhered onto the surface of the adhesive is too small, so that the adhesive may be exposed to the surface of each particle. When the amount of the carbon black fine particles added is more than 30 parts by weight, the obtained black magnetic acicular composite particles tend to suffer from desorption of carbon black from the surfaces thereof, resulting in deteriorated dispersibility in vehicle.

In the present invention, after carbon black is adhered onto the core particles, the obtained black magnetic acicular composite particles may be dried or heat-treated. The temperature used in the drying or heat-treatment, is preferably 40 to 200°C, more preferably 60 to 150°C, and the heating time is preferably from 10 minutes to 12 hours, more preferably from 30 minutes to 3 hours. By conducting such drying or heat-treatment, the alkoxysilane can be converted into organosilane compounds.

The surface of the core particles may be coated with at least one compound selected from the group consisting of hydroxides of aluminum or the like, if required, in advance of mixing and stirring with the alkoxysilane compounds or the polysiloxanes.

The coating of the hydroxides of aluminum or the like may be conducted by adding an aluminum compound, a silicon compound or both the compounds to a water suspension in which the core particles are dispersed, followed by mixing

and stirring, and further adjusting the pH value of the suspension, if required, thereby coating the surfaces of the core particles with hydroxides of aluminum or the like. The thus obtained core particles coated with the hydroxides of aluminum or the like are then filtered out, washed with water, dried and pulverized. Further, the particles coated with the hydroxides of aluminum or the like may be subjected to post-treatments such as deaeration treatment and compaction treatment, if required.

As the aluminum compounds, there may be exemplified aluminum salts such as aluminum acetate, aluminum sulfate, aluminum chloride or aluminum nitrate, alkali aluminates such as sodium aluminate or the like.

The amount of the aluminum compound added is 0.01 to 20 % by weight (calculated as Al) based on the weight of the core particles. When the amount of the aluminum compound added is less than 0.01 % by weight, it may be difficult to sufficiently coat the surfaces of the core particles with hydroxides of aluminum or the like, thereby failing to improve the effective reduction of the carbon black desorption percentage. On the other hand, when the amount of the aluminum compound added is more than 20 % by weight, the coating effect is saturated and, therefore, it is meaningless to add such an excess amount of the aluminum compound.

As the silicon compounds, there may be exemplified #3 water glass, sodium orthosilicate, sodium metasilicate or

the like.

The amount of the silicon compound added is 0.01 to 20 % by weight (calculated as  $\text{SiO}_2$ ) based on the weight of the core particles. When the amount of the silicon compound added is less than 0.01 % by weight, it may be difficult to sufficiently coat the surfaces of the core particles with oxides of silicon or the like, thereby failing to improve the effective reduction of the carbon black desorption percentage. On the other hand, when the amount of the silicon compound added is more than 20 % by weight, the coating effect is saturated and, therefore, it is meaningless to add such an excess amount of the silicon compound.

In the case where both the aluminum and silicon compounds are used in combination for the coating, the total amount of the aluminum and silicon compounds added is preferably 0.01 to 20 % by weight (calculated as a sum of Al and  $\text{SiO}_2$ ) based on the weight of the core particles.

Next, the process for producing the magnetic recording medium according to the present invention is described.

The magnetic recording medium according to the present invention can be produced by an ordinary method, i.e., by coating the surface of the non-magnetic base film with a non-magnetic coating composition comprising non-magnetic particles, a binder resin and a solvent to form a coating film thereon; drying the coating film to form a non-magnetic undercoat layer; coating the surface of the non-magnetic

undercoat layer with a magnetic coating composition comprising black magnetic acicular composite particles, a binder resin and a solvent to form a magnetic recording layer thereon, and then magnetically orienting the magnetic recording layer.

Upon kneading and dispersing the non-magnetic coating composition and magnetic coating composition, as kneaders, there may be used, for example, twin-screw kneader, twin-screw extruder, pressure kneader, twin-roll mill, triple-roll mill or the like; and as dispersing devices, there may be used ball mill, sand grinder, attritor, disper, homogenizer, ultrasonic dispersing device or the like.

The coating of the non-magnetic coating composition and magnetic coating composition may be conducted using gravure coater, reverse-roll coater, slit coater, die coater or the like. The thus obtained coating film may be magnetically oriented using counter magnet, solenoid magnet or the like.

As the solvents, there may be used methyl ethyl ketone, toluene, cyclohexanone, methyl isobutyl ketone, tetrahydrofuran, a mixture of these solvents or the like.

The total amount of the solvent used is 65 to 1,000 parts by weight based on 100 parts by weight of the black magnetic acicular composite particles. When the amount of the solvent used is less than 65 parts by weight, the viscosity of the magnetic coating composition prepared therefrom becomes too high, thereby making it difficult to

apply the magnetic coating composition. On the other hand, when the amount of the solvent used is more than 1,000 parts by weight, the amount of the solvent volatilized during the formation of the coating film becomes too large, thereby rendering the coating process industrially disadvantageous.

#### EMBODIMENT FOR CARRYING OUT THE INVENTION

The embodiment for carrying out the present invention will now be described in more detail.

The average major axial diameter and the average minor axial diameter of core particles or black magnetic acicular composite particles and average particle diameter of carbon black fine particles were respectively expressed by the average of values (measured in a predetermined direction) of about 350 particles which were sampled from a micrograph obtained by magnifying an original electron micrograph ( $\times 30,000$ ) by four times in each of the longitudinal and transverse directions.

The aspect ratio of the particles was expressed by the ratio of average major axial diameter to average minor axial diameter thereof.

The geometrical standard deviation of major axial diameter was expressed by values obtained by the following method. That is, the major axial diameters were measured from the above magnified electron micrograph. The actual major axial diameter and the number of the particles were



calculated from the measured values. On a logarithmic normal probability paper, the major axial diameters were plotted at regular intervals on the abscissa-axis and the accumulative number (under integration sieve) of particles belonging to each interval of the major axial diameter were plotted by percentage on the ordinate-axis by a statistical technique.

The major axial diameter corresponding to the number of particles of 50 % and 84.13 %, respectively, were read from the graph, and the geometrical standard deviation was calculated from the following formula:

$$\text{Geometrical standard deviation} = \frac{\{\text{major axial diameter corresponding to 84.13 \% under integration sieve}\} / \{\text{major axial diameter (geometrical average diameter) corresponding to 50 \% under integration sieve}\}}$$

The closer to 1 the geometrical standard deviation value, the more excellent the major axial diameter distribution.

The specific surface area was expressed by the value measured by a BET method.

The amount of Al, Si and Co which were present within core particles or black magnetic acicular composite particles, or on surfaces thereof, and the amount of Si

contained in the organosilane compounds obtainable from alkoxyasilane compounds, polysiloxanes or dimethyl polysiloxane coated on the surface of the black magnetic acicular composite particles were measured by a fluorescent X-ray spectroscopy device 3063 M (manufactured by Rigaku Denki Kogyo Co., Ltd.) according to JIS K0119 "General rule of fluorescent X-ray analysis".

The content of  $\text{Fe}^{2+}$  in the core particles is expressed by the value measured by the following chemical analysis method.

That is, 25 ml of a mixed solution composed of phosphoric acid and sulfuric acid at a mixing ratio of 2:1, was added to 0.5 g of core particles, thereby dissolving the core particles in the mixed solution. After several droplets of diphenylamine sulfonic acid as an indicator was added to the diluted solution, the solution was subjected to oxidation-reduction titration using an aqueous potassium bichromate solution. The titration was terminated when the diluted solution exhibited a violet color. The amount of  $\text{Fe}^{2+}$  was measured from the amount of the aqueous potassium bichromate solution used up to the termination of the titration.

The amount of carbon black coat formed on the surface of the black magnetic acicular composite particles was measured by "Horiba Metal, Carbon and Sulfur Analyzer EMIA-2200 Model" (manufactured by Horiba Seisakusho Co., Ltd.).

The blackness of the core particles, black magnetic acicular composite particles and carbon black was measured by the following method. That is, 0.5 g of sample particles and 1.5 ml of castor oil were intimately kneaded together by a Hoover's muller to form a paste. 4.5 g of clear lacquer was added to the obtained paste and was intimately kneaded to form a paint. The obtained paint was applied on a cast-coated paper by using a 6-mil applicator to produce a coating film piece (having a film thickness of about 30  $\mu\text{m}$ ). The thus obtained coating film piece was measured according to JIS Z 8729 by a multi-light source spectrographic colorimeter MSC-IS-2D (manufactured by Suga Testing Machines Manufacturing Co., Ltd.) to determine an  $L^*$  value of colorimetric indices thereof. The blackness was expressed by the  $L^*$  value measured.

Here, the  $L^*$  value represents a lightness, and the smaller the  $L^*$  value, the more excellent the blackness.

The volume resistivity of the core particles and black magnetic acicular composite particles was measured by the following method.

That is, first, 0.5 g of the sample particles to be measured was weighted, and press-molded at 140  $\text{Kg/cm}^2$  (13,720 kPa) using a KBr tablet machine (manufactured by Simazu Seisakusho Co., Ltd.), thereby forming a cylindrical test piece.

Next, the thus obtained cylindrical test piece was exposed to an atmosphere maintained at a temperature of 25°C

and a relative humidity of 60 % for 12 hours. Thereafter, the cylindrical test piece was set between stainless steel electrodes, and a voltage of 15V was applied between the electrodes using a Wheatstone bridge (model 4329A, manufactured by Yokogawa-Hokushin Denki Co., Ltd.) to measure a resistance value  $R$  ( $\Omega$ ).

The cylindrical test piece was measured with respect to an upper surface area  $A$  ( $\text{cm}^2$ ) and a thickness  $t_0$  (cm) thereof. The measured values were inserted into the following formula, thereby obtaining a volume resistivity  $X$  ( $\Omega\cdot\text{cm}$ ).

$$X (\Omega\cdot\text{cm}) = R \times (A/t_0)$$

The thickness of carbon black coat formed on the surfaces of the black magnetic acicular composite particles is expressed by the value which was obtained by first measuring an average thickness of carbon black coat formed onto the surfaces of the particles on a photograph ( $\times 5,000,000$ ) obtained by magnifying (ten times) a micrograph ( $\times 500,000$ ) produced at an accelerating voltage of 200 kV using a transmission-type electron microscope (JEM-2010, manufactured by Japan Electron Co., Ltd.), and then calculating an actual thickness of carbon black coat formed from the measured average thickness.

The desorption percentage (%) of carbon black desorbed from the black magnetic acicular composite particles was measured by the following method. The closer to zero the

desorption percentage (T %), the smaller the amount of carbon black desorbed from the sample particles.

That is, 3 g of the sample particles and 40 ml of ethanol were placed in a 50-ml precipitation pipe and then was subjected to ultrasonic dispersion for 20 minutes. Thereafter, the obtained dispersion was allowed to stand for 120 minutes, and separated the carbon black desorbed from the sample particles on the basis of the difference in specific gravity therebetween. Next, the thus separated sample particles were mixed again with 40 ml of ethanol, and the obtained mixture was further subjected to ultrasonic dispersion for 20 minutes. Thereafter, the obtained dispersion was allowed to stand for 120 minutes, thereby separating the sample particles and carbon black desorbed, from each other. The thus separated black magnetic acicular composite particles were dried at 100°C for one hour, and then the carbon content thereof was measured by the "Horiba Metal, Carbon and Sulfur Analyzer EMIA-2200 Model" (manufactured by HORIBA SEISAKUSHO CO., LTD.). The desorption percentage (T %) was calculated according to the following formula:

$$T (\%) = \{(W_a - W_e)/W_a\} \times 100$$

wherein  $W_a$  represents an amount of carbon black initially formed on the sample particles; and  $W_e$  represents an amount of carbon black which still remains on the sample particles after the above desorption test.

The myristic acid absorption of the magnetic acicular particles and the black magnetic acicular composite particles was measured by the following method. The lower the myristic acid absorption, the more the fatty acid becomes to ooze on the surface of the magnetic recording layer and the lower the friction coefficient thereof.

100 g of 1.5 mm $\phi$  glass beads, 9 g of sample particles to be measured and 45 ml of a tetrahydrofuran solution containing myristic acid in an amount enough to form one layer thereof on each sample particle, were charged into a 140-ml glass bottle, and then mixed and dispersed together for 60 minutes using a paint shaker.

Next, the thus obtained dispersion was taken out, charged into a 50-ml precipitation tube and centrifuged at 10,000 rpm for 15 minutes, thereby separating a solvent portion from a solid portion. The amount (concentration) of myristic acid contained in the solvent portion was determined by a gravimetric method. By subtracting the measured value from an amount of myristic acid initially charged, the amount of myristic acid contained in the solid portion was obtained as a myristic acid absorption (mg/m<sup>2</sup>) of the particles to be measured

The viscosity of the coating composition was obtained by measuring the viscosity of the coating composition at 25°C at a shear rate D of 1.92 sec<sup>-1</sup> by using "E type viscometer EMD-R" (manufactured by Tokyo Keiki, Co., Ltd.).

The gloss of the surface of the coating film of the magnetic recording layer was measured at an angle of incidence of  $45^{\circ}$  by "glossmeter UGV-5D" (manufactured by Suga Shikenki, Co., Ltd.).

The surface roughness Ra is expressed by the average value of the center-line average roughness of the profile curve of the surface of the coating film of the magnetic recording layer by using "Surfcom-575A" (manufactured by Tokyo Seimitsu Co., Ltd.).

The strength of the coating film was expressed the Young's modulus obtained by "Autograph" (produced by Shimazu Seisakusho Co., Ltd.). The Young's modulus was expressed by the ratio of the Young's modulus of the coating film to that of a commercially available video tape "AV T-120" (produce by Victor Company of Japan, Limited). The higher the relative value, the more favorable.

The magnetic properties of the core particles, black magnetic acicular composite particles and magnetic recording medium were measured under an external magnetic field of 10 kOe by "Vibration Sample Magnetometer VSM-3S-15 (manufactured by Toei Kogyo, Co., Ltd.)".

The light transmittance is expressed by the linear adsorption coefficient calculated by substituting the light transmittance measured by using "UV-Vis Recording Spectrophotometer UV-2100" (manufactured by Shimazu

Seisakusho, Ltd.) for the following formula. The larger the value, the more difficult it is for the magnetic recording medium to transmit light:

Linear adsorption coefficient ( $\mu\text{m}^{-1}$ ) =  $\{1 \text{ n } (1/t)\}/\text{FT}$   
wherein t represents a light transmittance (-) at  $\lambda = 900$  nm, and FT represents thickness ( $\mu\text{m}$ ) of the coating film used for the measurement.

The surface electrical resistivity of the coating film of the magnetic recording layer was measured by the following method. That is, the coating film to be measured was exposed to the environment maintained at a temperature of 25°C and a relative humidity of 60 %, for not less than 12 hours. Thereafter, the coating film was slit into 6 mm width, and the slit coating film was placed on two metal electrodes having a width of 6.5 mm such that a coating surface thereof was contacted with the electrodes. 1.7 N (170 gw) were respectively suspended at opposite ends of the coating film so as to bring the coating film into close contact with the electrodes. D.C. 500 V was applied between the electrodes, thereby measuring the surface electrical resistivity of the coating film.

The friction coefficient of the magnetic recording medium was determined by measuring a frictional force between a surface of the magnetic tape and a metal surface (aluminum polished surface) using a tensile tester TENSILON (manufactured by Shimadzu Seisakusho Co., Ltd.), and



expressed by the ratio of the measured value to the load.

The running durability was evaluated by the actual operating time under the conditions that the load was 1.96 N (200 gw) and the relative speed of the head and the tape was 16 m/s by using "Media Durability Tester MDT-3000" (manufactured by Steinberg Associates). The longer the actual operating time, the higher the running durability.

The thickness of each of the non-magnetic base film, the non-magnetic undercoat layer and the magnetic recording layer constituting the magnetic recording medium was measured in the following manner by using "Digital Electronic Micrometer R351C" (manufactured by Anritsu Corp.)

The thickness (A) of a base film was first measured. Similarly, the thickness (B) (B = the sum of the thicknesses of the base film and the non-magnetic undercoat layer) of a non-magnetic substrate obtained by forming a non-magnetic undercoat layer on the base film was measured. Furthermore, the thickness (C) (C = the sum of the thicknesses of the base film, the non-magnetic undercoat layer and the magnetic recording layer) of a magnetic recording medium obtained by forming a magnetic recording layer on the non-magnetic substrata was measured. The thickness of the non-magnetic undercoat layer is expressed by  $(B) - (A)$ , and the thickness of the magnetic recording layer is expressed by  $(C) - (B)$ .

<Production of black magnetic acicular composite particles>

20 kg of acicular cobalt-coated magnetite particles (cobalt content: 2.33 % by weight based on the weight of the acicular cobalt-coated magnetite particles;  $\text{Fe}^{2+}$  content: 15.4 % by weight based on the weight of the acicular cobalt-coated magnetite particles; average major axis diameter:  $0.270 \mu\text{m}$ ; average minor axis diameter:  $0.0329 \mu\text{m}$ ; aspect ratio: 8.2:1; geometrical standard deviation value: 1.36; BET specific surface area value:  $38.9 \text{ m}^2/\text{g}$ ; blackness ( $L^*$  value): 22.5; volume resistivity:  $7.4 \times 10^7 \cdot \text{cm}$ ; myristic acid absorption:  $0.79 \text{ mg}/\text{m}^2$ ; coercive force value: 698 Oe; saturation magnetization value:  $80.6 \text{ emu}/\text{g}$ ), were deagglomerated in 150 liters of pure water using a stirrer, and further passed through a "TK pipeline homomixer" (tradename, manufactured by Tokushu Kika Kogyo Co., Ltd.) three times, thereby obtaining a slurry containing the acicular cobalt-coated magnetite particles.

Successively, the obtained slurry containing the acicular cobalt-coated magnetite particles was passed through a transverse-type sand grinder (tradename "MIGHTY MILL MHG-1.5L", manufactured by Inoue Seisakusho Co., Ltd.) five times at an axis-rotating speed of 2,000 rpm, thereby obtaining a slurry in which the acicular cobalt-coated magnetite particles were dispersed.

The particles in the obtained slurry which remained on a sieve of 325 meshes (mesh size:  $44 \mu\text{m}$ ) was 0 %. The slurry was filtered and washed with water, thereby obtaining a filter cake containing the acicular cobalt-coated

magnetite particles. After the obtained filter cake containing the acicular cobalt-coated magnetite particles was dried at 120°C, 11.0 kg of the dried particles were then charged into an edge runner "MPUV-2 Model" (tradename, manufactured by Matsumoto Chuzo Tekkosho Co., Ltd.), and mixed and stirred at 30 Kg/cm and a stirring speed of 22 rpm for 15 minutes, while introducing nitrogen gas thereinto at a rate of 2 liter/minute, thereby lightly deagglomerating the particles.

165 g of methyltriethoxysilane (tradename: "TSL8123", produced by TOSHIBA SILICONE CO., LTD.) was mixed and diluted with 200 ml of ethanol to obtain a methyltriethoxysilane solution. The methyltriethoxysilane solution was added to the deagglomerated acicular cobalt-coated magnetite particles under the operation of the edge runner. The acicular cobalt-coated magnetite particles were continuously mixed and stirred at a linear load of 40 Kg/cm and a stirring speed of 22 rpm for 20 minutes.

Next, 825 g of carbon black fine particles B (particle shape: granular shape; average particle size: 0.022  $\mu\text{m}$ ; geometrical standard deviation value: 1.78; BET specific surface area value: 133.5  $\text{m}^2/\text{g}$ ; and blackness ( $L^*$  value): 14.6) were added to the acicular cobalt-coated magnetite particles coated with methyltriethoxysilane for 10 minutes while operating the edge runner. Further, the mixed particles were continuously stirred at a linear load of 30 Kg/cm and a stirring speed of 22 rpm for 30 minutes to form

the carbon black coat on the coating layer composed of methyltriethoxysilane, thereby obtaining black magnetic acicular composite particles.

The obtained black magnetic acicular composite particles were heat-treated at 80°C for 120 minutes by using a drier. As shown in the electron micrograph, the resultant black magnetic acicular composite particles had an average major axis diameter of 0.273  $\mu\text{m}$ , an average minor axis diameter of 0.0331  $\mu\text{m}$ , an aspect ratio of 8.2:1. In addition, the black magnetic acicular composite particles showed a geometrical standard deviation value of 1.36, a BET specific surface area value of 40.2  $\text{m}^2/\text{g}$ , a blackness ( $L^*$  value) of 19.7 and a volume resistivity of  $9.8 \times 10^4 \cdot \cdot \text{cm}$ , and a carbon black desorption percentage of 7.8 %. As to the magnetic properties, the coercive force value of the black magnetic acicular composite particles was 682 Oe and the saturation magnetization value was 79.3 emu/g.

Further, it was confirmed that the total amount of carbon black adhered and bonded was 6.88 % by weight (calculated as C; corresponding to 7.5 parts by weight based on 100 parts by weight of the core particles); and the coating amount of methyltriethoxysilane was 0.22 % by weight (calculated as Si). Meanwhile, as a result of the observation by electron microscope, it was recognized that since substantially no liberated carbon black was observed, almost whole amount of carbon black added was adhered onto the coating layer of organosilane compounds produced from

methyltriethoxysilane.

It was confirmed that the thickness of carbon black coat on the surface of each particle was  $0.0018 \mu\text{m}$ .

For a comparative purpose, the acicular cobalt-coated magnetite particles not coated with methyltriethoxysilane and the carbon black fine particles were mixed and stirred together by an edge runner in the same manner as described above, thereby obtaining treated particles as shown in the electron photograph. As shown in the electron photograph, it was recognized that the carbon black fine particles were not adhered on the acicular cobalt-coated magnetite particles, and the individual particles were present separately.

<Production of non-magnetic undercoat layer>

12 g of non-magnetic particles 1 shown in Table 9 below (kind: hematite particles; particle shape: spindle-shaped; average major axial diameter:  $0.187 \mu\text{m}$ ; average minor axial diameter:  $0.0240 \mu\text{m}$ ; aspect ratio: 7.8:1; geometrical standard deviation value: 1.33; BET specific surface area value:  $43.3 \text{ m}^2/\text{g}$ ; volume resistivity value:  $8.6 \times 10^8 \text{ } \Omega\cdot\text{cm}$ ; blackness ( $L^*$  value): 32.6) were mixed with a binder resin solution (containing 30 % by weight of vinyl chloride-vinyl acetate copolymer resin having a sodium sulfonate group and 70 % by weight of cyclohexanone) and cyclohexanone, thereby obtaining a mixture (solid content: 72 %). The obtained mixture was further kneaded for 30 minutes using a plastomill, thereby obtaining a kneaded

material.

The thus obtained kneaded material was added to a 140ml glass bottle together with 95 g of 1.5mm $\phi$  glass beads, an additional amount of a binder resin solution (containing 30 % by weight of polyurethane resin having a sodium sulfonate group and 70% by weight of a mixed solvent of methyl ethyl ketone and toluene (1:1)), cyclohexanone, methyl ethyl ketone and toluene. The resultant mixture was mixed and dispersed for 6 hours by a paint shaker, thereby obtaining a coating composition. Thereafter, a lubricant was added to the obtained coating composition, and the mixture was mixed and dispersed for 15 minutes by a paint shaker.

The composition of the obtained non-magnetic coating composition was as follows:

Non-magnetic particles 1	100 parts by
weight	
Vinyl chloride-vinyl acetate	
copolymer resin having	
a sodium sulfonate group	10 parts by weight
Polyurethane resin having	
a sodium sulfonate group	10 parts by weight
Lubricant (myristic acid:	
butyl stearate = 1:1)	2 parts by weight
Cyclohexanone	56.9 parts by weight
Methyl ethyl ketone	142.3 parts by weight
Toluene	85.4 parts by weight

The obtained non-magnetic coating composition had a viscosity of 310 cP.

Next, the non-magnetic coating composition was coated on a 12  $\mu\text{m}$ -thick polyethylene terephthalate film using an applicator so as to form thereon a 55  $\mu\text{m}$ -thick coating layer, and then dried, thereby producing a non-magnetic undercoat layer.

The thus obtained non-magnetic undercoat layer had a thickness of 3.4  $\mu\text{m}$ , and exhibited a gloss of 193%, a surface roughness Ra of 8.2 nm, a Young's modulus (relative value) of 123, a linear absorption of  $1.01 \mu\text{m}^{-1}$  and a surface electrical resistivity value of  $1.1 \times 10^{14} \text{ } \Omega \cdot \text{cm}$ .

<Production of magnetic recording medium: Formation of magnetic recording layer>

12 g of the thus obtained black magnetic acicular composite particles, 1.2 g of a polishing agent (AKP-30: trade name, produced by Sumitomo Chemical Co., Ltd.), 0.06 g of carbon black fine particles (#2400B, trade name, produced by Mitsubishi Chemical Corp.), a binder resin solution (30 % by weight of vinyl chloride-vinyl acetate copolymer resin having a sodium sulfonate group and 70 % by weight of cyclohexanone) and cyclohexanone were mixed to obtain a mixture (solid content: 78 % by weight). The mixture was further kneaded by a plast-mill for 30 minutes to obtain a kneaded material.

The thus-obtained kneaded material was charged into a 140 ml-glass bottle together with 95 g of 1.5 mmφ glass beads, a binder resin solution (30 % by weight of polyurethane resin having a sodium sulfonate group and 70 % by weight of a solvent (methyl ethyl ketone : toluene = 1 : 1)), cyclohexanone, methyl ethyl ketone and toluene, and the mixture was mixed and dispersed by a paint shaker for 6 hours. Then, the lubricant and hardening agent were added to the mixture, and the resultant mixture was mixed and dispersed by a paint shaker for 15 minutes.

The thus-obtained magnetic coating composition was as follows:

Black magnetic acicular composite particles	100 parts by weight
Vinyl chloride-vinyl acetate copolymer resin having a sodium sulfonate group	10 parts by weight
Polyurethane resin having a sodium sulfonate group	10 parts by weight
Polishing agent (AKP-30)	10 parts by weight
Carbon black fine particles (#2400B)	0.5 parts by weight
Lubricant (myristic acid: butyl stearate = 1 : 2)	3.0 parts by weight
Hardening agent (polyisocyanate)	5.0 parts by weight
Cyclohexanone	65.8 parts by weight



Methyl ethyl ketone	164.5 parts by weight
Toluene	98.7 parts by weight

The viscosity of the obtained magnetic coating composition was 2,338 cP.

The magnetic coating composition obtained was applied to the above-mentioned non-magnetic undercoat layer to a thickness of 15  $\mu\text{m}$  by an applicator, and the magnetic recording medium obtained was oriented and dried in a magnetic field, and then calendered. The magnetic recording medium was then subjected to a curing reaction at 60°C for 24 hours, and thereafter slit into a width of 0.5 inch, thereby obtaining a magnetic tape. The thickness of the respective magnetic recording layer was 3.4  $\mu\text{m}$ .

The coercive force value of the magnetic tape produced by forming a magnetic recording layer on the non-magnetic base film was 746 Oe, the squareness (Br/Bm) thereof was 0.89, the gloss thereof was 174 %, the surface roughness Ra thereof was 7.4 nm, the Young's modulus (relative value) thereof was 138, the linear absorption coefficient thereof was  $1.54 \mu\text{m}^{-1}$ , and the surface electrical resistivity was  $5.3 \times 10^7 \text{ } \Omega/\text{cm}^2$ . Further, as to the durability of the magnetic tape, the running durability time was not less than 29.5 minutes.

#### FUNCTION:

The important point of the present invention is the fact that the magnetic recording medium which is obtained by

using the black magnetic acicular composite particles as magnetic particles, can exhibit a small light transmittance and a low surface electrical resistivity value even though the amount of carbon black incorporated in a magnetic recording layer thereof is reduced to as small a level as possible, and can be enhanced in surface smoothness of the magnetic recording layer.

The reason why the magnetic recording medium of the present invention can show a small light transmittance irrespective of a less amount of carbon black added thereto, is considered by the present inventors as follows. That is, carbon black fine particles usually tend to form agglomerates due to fineness thereof. However, in the black magnetic acicular composite particles of the present invention, since the carbon black fine particles can be uniformly and densely adhered onto the surfaces of the core particles, the individual carbon black fine particles can exhibit a function thereof more effectively.

The reason why the magnetic recording medium of the present invention can show a low surface electrical resistivity value irrespective of a less amount of carbon black added thereto, is considered by the present inventors as follows. That is, since the black magnetic acicular composite particles are uniformly dispersed in the coating film, the carbon black fine particles uniformly and densely adhered onto the surfaces of the respective composite particles are continuously connected and contacted with each

other in the coating film.

The reason why the magnetic recording medium of the present invention can show an excellent surface smoothness, is considered by the present inventors as follows. That is, in the black magnetic acicular composite particles of the present invention, the amount of carbon black fine particles desorbed or fallen-off from the surfaces of the particles is very small, and the amount of carbon black fine particles added into the magnetic recording layer of the magnetic recording medium can be reduced to as small a level as possible. For these reasons, the black magnetic acicular composite particles are prevented from being deteriorated in dispersibility in vehicle due to desorbed and liberated carbon black fine particles upon the production of magnetic coating composition. Further, the black magnetic acicular composite particles themselves are excellent in dispersibility in vehicle.

The magnetic recording medium according to the present invention in which the black magnetic acicular composite particles having a well-controlled myristic acid-adsorption are used, can exhibit a low friction coefficient and an excellent running durability.

The reason why the magnetic recording medium according to the present invention can be reduced in friction coefficient, is considered by the present inventors as follows. That is, by controlling the amount of myristic acid adsorbed onto the surfaces of the black magnetic

acicular composite particles which are incorporated in a large amount into a magnetic recording layer of the magnetic recording medium, to the specified range, an appropriate amount of myristic acid can be oozed onto the surface of the magnetic recording layer in a well-controlled condition for a long period of time, thereby effectively exhibiting a good lubricating function thereof.

The reason why the magnetic recording medium of the present invention has an excellent running durability, is considered by the present inventors as follows. That is, for the same reason as described above, an appropriate amount of myristic acid can be oozed onto the surface of the magnetic recording layer in a well-controlled condition, resulting in stable running durability of the magnetic recording medium.

#### EXAMPLES

The present invention is described in more detail by Examples and Comparative Examples.

#### Core particles 1 to 5:

Various core particles were prepared by known methods. The same procedure as defined in Embodiment for Carrying out the Present Invention was conducted by using the thus magnetic acicular particles, thereby obtaining deagglomerated magnetic acicular particles as core particles.

Various properties of the thus obtained magnetic acicular particles are shown in Table 1.

Core particles 6:

The same procedure as defined in Embodiment for Carrying out the Present Invention was conducted by using 20 kg of the deagglomerated acicular cobalt-coated maghemite particles (core particles 1) and 150 liters of water, thereby obtaining a slurry containing the acicular cobalt-coated maghemite particles. The pH value of the obtained re-dispersed slurry containing the acicular cobalt-coated maghemite particles was adjusted to 10.5 by adding an aqueous sodium hydroxide solution, and then the concentration of the slurry was adjusted to 98 g/liter by adding water thereto. After 150 liters of the slurry was heated to 60°C, 5,444 ml of a 1.0 mol/liter sodium aluminate solution (equivalent to 1.0 % by weight (calculated as Al) based on the weight of the acicular cobalt-coated maghemite particles) was added to the slurry. After allowing the slurry to stand for 30 minutes, the pH value of the slurry was adjusted to 7.5 by adding an aqueous acetic acid solution. After further allowing the slurry to stand for 30 minutes, the slurry was subjected to filtration, washing with water, drying and pulverization, thereby obtaining the acicular cobalt-coated maghemite particles coated with hydroxides of aluminum.

Main production conditions are shown in Table 2, and

various properties of the obtained acicular cobalt-coated maghemite particles are shown in Table 3.

Core particles 7 to 10:

The same procedure as defined in the production of the core particles 6 above, was conducted except that kind of core particles, and kind and amount of additives used in the surface treatment were varied, thereby obtaining surface-treated magnetic acicular particles.

Main production conditions are shown in Table 2, and various properties of the obtained surface-treated magnetic acicular particles are shown in Table 3.

In Table 2, "A" denotes a hydroxide of aluminum and "S" denotes an oxide of silicon.

<Production of black magnetic acicular composite particles>

Examples 1 to 12 and Comparative Examples 1 to 5:

The same procedure as defined in Embodiment for Carrying out the Present Invention was conducted except that kind of core particles, addition or non-addition, kind and amount of alkoxysilane, polysiloxane or silicon compound upon the coating step, edge runner treatment conditions used in the coating step, kind and amount of carbon black fine particles added in the carbon black coat forming steps and edge runner treatment conditions used in the carbon black coat forming steps, were changed variously, thereby obtaining black magnetic acicular composite particles. As a

result of observing the black magnetic acicular composite particles obtained in Examples 1 to 12 by an electron microscope, substantially no liberated carbon black was recognized. Therefore, it was confirmed that almost whole amount of carbon black coat was formed onto the coating layer of organosilane compounds produced from alkoxysilane, or the coating layer of polysiloxane.

Various properties of the carbon black fine particles B to F used, are shown in Table 4. The essential treating conditions are shown in Table 5, and various properties of the obtained black magnetic acicular composite particles are shown in Table 6.

Meanwhile, all the additives used in Examples 8 to 10 were polysiloxanes. Specifically, "TSF484" (tradename, produced by Toshiba Silicone Co., Ltd.) was methyl hydrogen polysiloxane; "BYK-080" (tradename, produced by BYK-Chemie Japan Co., Ltd.) was modified polysiloxane; and "TSF-4770" (tradename, produced by Toshiba Silicone Co., Ltd.) was terminal carboxyl group-modified polysiloxane.

<Production of black magnetic acicular composite particles adhering carbon black in a large amount>

Examples 13

5.0 kg of the obtained black magnetic acicular composite particles in Example 38 were charged into an edge runner "MPUV-2 Model" (tradename, manufactured by Matsumoto Chuzo Tekkosho Co., Ltd.), and then mixed and stirred at a

linear load of 30 Kg/cm for 30 minutes, thereby lightly deaggregating the particles.

Then, 100 g of dimethyl polysiloxane was added to the black magnetic acicular composite particles while operating the edge runner, and mixed and stirred together at a linear load of 30 Kg/cm for 30 minutes, thereby obtaining black magnetic acicular composite particles on the surfaces of which dimethyl polysiloxane was uniformly adhered.

Then, 500 g of the above carbon black fine particles B were added to the thus obtained black magnetic acicular composite particles for 10 minutes while operating the edge runner, and further mixed and stirred together at linear load of 45 Kg/cm and a stirring speed of 22 rpm for 30 minutes to form a second carbon black coat onto the surface of the first carbon black coat through dimethyl polysiloxane as an adhesive, thereby obtaining black magnetic acicular composite particles.

The thus obtained black magnetic acicular composite particles were dried at 105°C for 60 minutes using a dryer. As a result of the observation by electron microscope, it was confirmed that the thus obtained black magnetic acicular composite particles had an average major axis diameter of 0.278  $\mu\text{m}$ , an average minor axis diameter of 0.0341  $\mu\text{m}$ , an aspect ratio of 8.2:1. In addition, the black magnetic acicular composite particles showed a geometrical standard deviation value of 1.37, a BET specific surface area value of 43.5  $\text{m}^2/\text{g}$ , a blackness ( $L^*$  value) of 18.6 and a volume



resistivity of  $2.1 \times 10^4 \cdot \text{cm}$ , a myristic acid-adsorption of  $0.27 \text{ mg/m}^2$  and a carbon black desorption percentage of 7.6 %. As to the magnetic properties, the coercive force value of the black magnetic acicular composite particles was 675 Oe and the saturation magnetization value was  $77.4 \text{ emu/g}$ .

Further, it was confirmed that the total amount of carbon black adhered and bonded was 14.62 % by weight (calculated as C; corresponding to 17.5 parts by weight based on 100 parts by weight of the core particles); the coating amount of dimethyl polysiloxane was 0.71 % by weight (calculated as Si). Meanwhile, as a result of the observation by electron microscope, substantially no liberated carbon black was recognized. Therefore, it was confirmed that almost whole amount of the carbon black added was adhered onto the first carbon black coat.

It was confirmed that the thickness of carbon black adhered on the surface of each particle was  $0.0020 \text{ }\mu\text{m}$ .

Examples 14 to 25 and Comparative Examples 6 to 12:

The same procedure as defined in Example 13 was conducted except that kind of black magnetic acicular composite particles, kind and amount of adhesive added in the bonding step, edge runner treatment conditions used in the bonding step, kind and amount of carbon black coat forming added in carbon black coat forming steps and edge runner treatment conditions used in the carbon black adhering steps, were changed variously, thereby obtaining

black magnetic acicular composite particles.

Meanwhile, as a result of observing the black magnetic acicular composite particles adhering obtained at a large amount, in Examples 14 to 25 by an electron microscope, substantially no liberated carbon black was recognized. Therefore, it was confirmed that almost whole amount of carbon black added was adhered onto the first carbon black coat.

Main treatment conditions are shown in Table 7, and various properties of the obtained black magnetic acicular composite particles are shown in Table 8.

<Production of non-magnetic undercoat layers>

Non-magnetic undercoat layers 1 to 6:

Non-magnetic undercoat layers were produced using various non-magnetic particles by the same method as defined in Embodiment for Carrying out the Present Invention.

Various properties of the non-magnetic particles 1 to 6 used above are shown in Table 9.

Main production conditions and various properties of the obtained non-magnetic undercoat layers are shown in Table 10.

<Production of magnetic recording medium>

Examples 26 to 50 and Comparative Examples 13 to 29:

The same procedure as defined in Embodiment for Carrying out the Present Invention was conducted except that

kind and amount of black magnetic acicular composite particles added, were changed variously, thereby producing magnetic recording media.

Production conditions and various properties of magnetic recording media are shown in Tables 11 to 13.

Table 1

Core particles	Kind of core particles	Properties of core particles
		Particle shape
Core particles 1	Cobalt-coated maghemite particles (Co content: 2.65 wt. %)	Acicular
Core particles 2	Cobalt-coated maghemite particles (Co content: 4.23 wt. %)	Spindle-shaped
Core particles 3	Cobalt-coated magnetite particles (Co content: 2.22 wt. %; Fe <sup>2+</sup> content: 15.9 wt. %)	Acicular
Core particles 4	Cobalt-coated magnetite particles (Co content: 4.79 wt. %; Fe <sup>2+</sup> content: 13.7 wt. %)	Spindle-shaped
Core particles 5	Magnetic metal particles containing iron as a main component (Al content: 2.80 wt. %; Co content: 5.64 wt. %)	Spindle-shaped

Table 1 (continued)

Core particles	Properties of core particles		
	Average major axial diameter ( $\mu\text{m}$ )	Average minor axial diameter ( $\mu\text{m}$ )	Aspect ratio (-)
Core particles 1	0.273	0.0334	8.2:1
Core particles 2	0.210	0.0285	7.4:1
Core particles 3	0.291	0.0359	8.1:1
Core particles 4	0.149	0.0220	6.8:1
Core particles 5	0.125	0.0175	7.1:1

Table 1 (continued)

Core particles	Properties of core particles		
	Geometrical standard deviation value (-)	BET specific surface area value ( $\text{m}^2/\text{g}$ )	Coercive force value (Oe)
Core particles 1	1.39	36.0	690
Core particles 2	1.36	40.4	843
Core particles 3	1.42	31.3	710
Core particles 4	1.45	52.9	911
Core particles 5	1.40	53.8	1,927

Table 1 (continued)

Core particles	Properties of core particles	
	Saturation magnetization value (emu/g)	Volume resistivity value (••cm)
Core particles 1	76.4	$6.5 \times 10^8$
Core particles 2	78.7	$3.6 \times 10^8$
Core particles 3	82.9	$9.2 \times 10^7$
Core particles 4	81.0	$5.1 \times 10^7$
Core particles 5	136.1	$2.1 \times 10^7$

Table 1 (continued)

Core particles	Properties of core particles	
	Blackness (L* value) (-)	Myristic acid adsorption (mg/m <sup>2</sup> )
Core particles 1	24.3	0.78
Core particles 2	25.6	0.83
Core particles 3	22.9	0.86
Core particles 4	22.8	0.88
Core particles 5	22.4	1.01



Table 2

Core particles	Kind of core particles	Surface-treatment step		
		Additives		
		Kind	Calculated as	Amount (wt. %)
Core particles 6	Core particles 1	Sodium aluminate	Al	1.0
Core particles 7	Core particles 2	Water glass #3	SiO <sub>2</sub>	0.75
Core particles 8	Core particles 3	Aluminum sulfate	Al	2.0
		Water glass #3	SiO <sub>2</sub>	0.5
Core particles 9	Core particles 4	Sodium aluminate	Al	3.0
Core particles 10	Core particles 5	Water glass #3	SiO <sub>2</sub>	5.0

Table 2 (continued)

Core particles	Surface-treatment step		
	Coating composition		
	Kind	Calculated as	Amount (wt. %)
Core particles 6	A	Al	0.98
Core particles 7	S	SiO <sub>2</sub>	0.72
Core particles 8	A	Al	1.93
	S	SiO <sub>2</sub>	0.46
Core particles 9	A	Al	2.80
Core particles 10	S	SiO <sub>2</sub>	4.74

Table 3

Core particles	Properties of surface-treated magnetic acicular particles		
	Average major axial diameter ( $\mu\text{m}$ )	Average minor axial diameter ( $\mu\text{m}$ )	Aspect ratio (-)
Core particles 6	0.273	0.0334	8.2:1
Core particles 7	0.210	0.0285	7.4:1
Core particles 8	0.292	0.0360	8.1:1
Core particles 9	0.150	0.0221	6.8:1
Core particles 10	0.126	0.0176	7.2:1

Table 3 (continued)

Core particles	Properties of surface-treated magnetic acicular particles		
	Geometrical standard deviation value (-)	BET specific surface area value ( $\text{m}^2/\text{g}$ )	Coercive force value (Oe)
Core particles 6	1.40	36.4	686
Core particles 7	1.35	40.9	834
Core particles 8	1.41	32.6	701
Core particles 9	1.45	54.8	900
Core particles 10	1.39	56.0	1,899

Table 3 (continued)

Core particles	Properties of surface-treated magnetic acicular particles	
	Saturation magnetization value (emu/g)	Volume resistivity value ( $\cdot\cdot\text{cm}$ )
Core particles 6	75.9	$7.2 \times 10^8$
Core particles 7	78.3	$4.5 \times 10^8$
Core particles 8	81.5	$1.8 \times 10^8$
Core particles 9	79.8	$8.6 \times 10^7$
Core particles 10	133.2	$4.3 \times 10^7$

Table 3 (continued)

Core particles	Properties of surface-treated magnetic acicular particles	
	Blackness (L* value) (-)	Myristic acid adsorption (mg/m <sup>2</sup> )
Core particles 6	24.3	0.57
Core particles 7	25.6	0.63
Core particles 8	23.3	0.56
Core particles 9	23.0	0.59
Core particles 10	22.6	0.76

Table 4

Kind of carbon black fine particles	Properties of carbon black fine particles		
	Particle shape	Average particle size ( $\mu\text{m}$ )	Geometrical standard deviation value (-)
Carbon black A	Granular	0.022	1.68
Carbon black B	Granular	0.022	1.78
Carbon black C	Granular	0.015	1.56
Carbon black D	Granular	0.030	2.06
Carbon black E	Granular	0.024	1.69
Carbon black F	Granular	0.028	1.71

Table 4 (continued)

Kind of carbon black fine particles	Properties of carbon black fine particles			
	BET specific surface area	pH value	DBP oil absorption	Blackness (L* value)
	value (m <sup>2</sup> /g)	(-)	(ml/100g)	(-)
Carbon black A	134.0	3.4	89	16.6
Carbon black B	133.5	3.4	84	14.6
Carbon black C	265.3	3.7	57	15.2
Carbon black D	84.6	8.0	95	17.0
Carbon black E	113.6	10.8	102	16.2
Carbon black F	800.0	7.0	200	15.3



Table 5

Examples and Comparative Examples	Kind of core particles	Production of black composite hematite particles	
		Coating with alkoxysilane	
		Additive	
		Kind	Amount added (part by weight)
Example 1	Core particles 1	Methyl triethoxysilane	1.0
Example 2	Core particles 2	Methyl trimethoxysilane	1.5
Example 3	Core particles 3	Dimethyl dimethoxysilane	2.5
Example 4	Core particles 4	Phenyl triethoxysilane	2.0
Example 5	Core particles 5	Isobutyl trimethoxysilane	3.0
Example 6	Core particles 6	Methyl triethoxysilane	1.5
Example 7	Core particles 7	Methyl trimethoxysilane	2.0
Example 8	Core particles 8	TSP484	1.0
Example 9	Core particles 9	BYK-080	1.0
Example 10	Core particles 10	TSP4770	1.0
Example 11	Core particles 1	Methyl triethoxysilane	2.5
Example 12	Core particles 1	Methyl triethoxysilane	2.0
Comparative Example 1	Core particles 1	-	-
Comparative Example 2	Core particles 1	Methyl triethoxysilane	0.005
Comparative Example 3	Core particles 1	Methyl trimethoxysilane	1.0
Comparative Example 4	Core particles 1	$\gamma$ -aminopropyl triethoxysilane	1.0
Comparative Example 5	Core particles 1	-	-

Table 5 (continued)

Examples and Comparative Examples	Production of composite particles		
	Coating step with alkoxyasilane, polysiloxane or silicon compound		
	Edge runner treatment		Coating amount (calculated as Si) (wt. %)
	Linear load (Kg/cm)	Time (min.)	
Example 1	30	30	0.14
Example 2	45	30	0.29
Example 3	60	30	0.55
Example 4	45	20	0.25
Example 5	40	25	0.44
Example 6	45	30	0.22
Example 7	60	20	0.39
Example 8	30	20	0.42
Example 9	30	30	0.17
Example 10	45	30	0.35
Example 11	60	20	0.37
Example 12	30	30	0.39
Comparative Example 1	-	-	-
Comparative Example 2	30	20	$7 \times 10^{-4}$
Comparative Example 3	30	20	0.15
Comparative Example 4	30	20	0.13
Comparative Example 5	-	-	-

Table 5 (continued)

Examples and Comparativ e Examples	Production of black composite hematite particles	
	Coating of carbon black	
	Carbon black	
	Kind	Amount added (part by weight)
Example 1	B	5.0
Example 2	B	7.5
Example 3	C	3.0
Example 4	C	10.0
Example 5	D	8.0
Example 6	D	10.0
Example 7	B	5.0
Example 8	C	7.5
Example 9	D	5.0
Example 10	B	3.0
Example 11	E	5.0
Example 12	F	5.0
Comparativ e Example 1	B	5.0
Comparativ e Example 2	C	5.0
Comparativ e Example 3	D	15.0
Comparativ e Example 4	D	5.0
Comparativ e Example 5	D	10.0

Table 5 (continued)

Examples and Comparativ e Examples	Production of black composite hematite particles		
	Coating of carbon black		
	Edge runner treatment		Amount coated (calculated as C) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 1	45	20	4.75
Example 2	60	30	6.93
Example 3	30	30	2.85
Example 4	60	20	9.00
Example 5	45	20	7.35
Example 6	40	25	9.01
Example 7	30	30	4.74
Example 8	60	20	6.92
Example 9	45	20	4.74
Example 10	60	20	2.82
Example 11	60	20	4.75
Example 12	60	20	4.73
Comparativ e Example 1	30	20	4.74
Comparativ e Example 2	30	20	4.73
Comparativ e Example 3	30	20	13.01
Comparativ e Example 4	30	20	4.68
Comparativ e Example 5	30	20	9.08



Table 6

Examples and Comparative Examples	Properties of black composite hematite particles			
	Average major axial diameter (average particle size) ( $\mu\text{m}$ )	Average minor axial diameter ( $\mu\text{m}$ )	Aspect ratio (-)	Geometrical standard deviation value (-)
Example 1	0.276	0.0336	8.2:1	1.40
Example 2	0.211	0.0288	7.3:1	1.35
Example 3	0.291	0.0360	8.1:1	1.43
Example 4	0.151	0.0224	6.7:1	1.43
Example 5	0.127	0.0179	7.1:1	1.39
Example 6	0.277	0.0338	8.2:1	1.40
Example 7	0.212	0.0288	7.4:1	1.36
Example 8	0.293	0.0362	8.1:1	1.43
Example 9	0.150	0.0221	6.8:1	1.45
Example 10	0.129	0.0180	7.2:1	1.39
Example 11	0.274	0.0337	8.1:1	1.40
Example 12	0.274	0.0337	8.1:1	1.40
Comparative Example 1	0.273	0.0334	8.2:1	-
Comparative Example 2	0.273	0.0334	8.2:1	-
Comparative Example 3	0.275	0.0338	8.1:1	-
Comparative Example 4	0.273	0.0334	8.2:1	-
Comparative Example 5	0.273	0.0334	8.2:1	-

Table 6 (continued)

Examples and Comparative Examples	Properties of black composite hematite particles		
	BET specific surface area value (m <sup>2</sup> /g)	Coercive force Value (Oe)	Saturation magnetization value (emu/g)
Example 1	38.6	677	72.4
Example 2	43.0	839	74.0
Example 3	32.2	702	80.1
Example 4	56.2	889	76.8
Example 5	55.9	1,914	132.0
Example 6	40.1	666	70.7
Example 7	42.4	831	74.1
Example 8	34.7	690	78.2
Example 9	55.7	885	76.9
Example 10	57.0	1,902	131.8
Example 11	38.1	683	72.9
Example 12	39.3	681	72.7
Comparative Example 1	41.8	678	72.5
Comparative Example 2	40.2	679	72.6
Comparative Example 3	42.9	672	72.3
Comparative Example 4	41.1	678	72.8
Comparative Example 5	45.6	674	72.4

Table 6 (continued)

Examples and Comparative Examples	Properties of black composite hematite particles		
	Volume resistivity value ( $\bullet \bullet \text{cm}$ )	Blackness ( $L^*$ value) (-)	Carbon black desorption percentage (%)
Example 1	$4.1 \times 10^4$	19.4	8.5
Example 2	$1.5 \times 10^5$	19.3	8.5
Example 3	$7.5 \times 10^5$	20.2	7.1
Example 4	$1.6 \times 10^5$	19.5	8.4
Example 5	$3.9 \times 10^5$	19.2	8.9
Example 6	$1.7 \times 10^4$	19.4	4.3
Example 7	$8.6 \times 10^4$	19.8	4.0
Example 8	$4.4 \times 10^5$	19.2	3.8
Example 9	$9.3 \times 10^4$	19.5	2.9
Example 10	$5.2 \times 10^5$	18.9	3.6
Example 11	$4.1 \times 10^4$	20.0	9.0
Example 12	$2.6 \times 10^4$	20.3	9.5
Comparative Example 1	$6.3 \times 10^7$	22.6	65.2
Comparative Example 2	$5.1 \times 10^7$	22.8	46.6
Comparative Example 3	$9.6 \times 10^6$	19.4	28.3
Comparative Example 4	$5.4 \times 10^7$	22.5	52.8
Comparative Example 5	$1.6 \times 10^7$	22.0	68.3



Table 7

Examples	Kind of core particles	Production of black magnetic acicular composite particles	
		Treating step with dimethyl polysiloxane	
		Additives	
		Kind	Amount added (part by weight)
Example 13	Embodiment for Carrying out	Dimethyl polysiloxane	2.0
Example 14	Example 1	Dimethyl polysiloxane	1.5
Example 15	Example 2	Dimethyl polysiloxane	1.5
Example 16	Example 3	Dimethyl polysiloxane	2.0
Example 17	Example 4	Dimethyl polysiloxane	3.0
Example 18	Example 5	Dimethyl polysiloxane	1.0
Example 19	Example 6	Dimethyl polysiloxane	1.0
Example 20	Example 7	Dimethyl polysiloxane	1.5
Example 21	Example 8	Dimethyl polysiloxane	2.0
Example 22	Example 9	Dimethyl polysiloxane	1.5
Example 23	Example 10	Dimethyl polysiloxane	2.0
Example 24	Example 11	Dimethyl polysiloxane	1.5
Example 25	Example 12	Dimethyl polysiloxane	1.0
Comparative Example 6	Comparative Example 1	Dimethyl polysiloxane	1.0
Comparative Example 7	Comparative Example 2	Dimethyl polysiloxane	1.0
Comparative Example 8	Comparative Example 3	Dimethyl polysiloxane	1.0
Comparative Example 9	Comparative Example 4	Dimethyl polysiloxane	1.0
Comparative Example 10	Example 1	-	-
Comparative Example 11	Example 1	Dimethyl polysiloxane	0.005
Comparative Example 12	Example 1	Methyl ethoxysilane	1.0

Table 7 (continued)

Examples and Comparative Examples	Production of black magnetic acicular composite particles		
	Treating step with dimethyl polysiloxane or silicon compound		
	Edge runner treatment		Coating amount (calculated as Si) (wt. %)
	Linear load (Kg/cm)	Time (min.)	
Example 13	30	30	0.71
Example 14	45	20	0.51
Example 15	75	20	0.50
Example 16	60	20	0.70
Example 17	40	25	1.01
Example 18	30	30	0.30
Example 19	45	30	0.31
Example 20	60	20	0.52
Example 21	60	20	0.70
Example 22	60	20	0.53
Example 23	45	30	0.72
Example 24	60	30	0.51
Example 25	30	25	0.30
Comparative Example 6	60	30	0.31
Comparative Example 7	60	30	0.30
Comparative Example 8	60	30	0.30
Comparative Example 9	60	30	0.31
Comparative Example 10	-	-	-
Comparative Example 11	30	20	$2 \times 10^{-3}$

Comparative Example 12	30	20	0.15
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Table 7 (continued)

Examples and Comparative Examples	Production of black magnetic acicular composite particles	
	Coat formation step with carbon black	
	Carbon black	
	Kind	Amount added (part by weight)
Example 13	B	10.0
Example 14	B	15.0
Example 15	C	5.0
Example 16	D	10.0
Example 17	B	15.0
Example 18	C	15.0
Example 19	D	10.0
Example 20	B	15.0
Example 21	C	7.5
Example 22	D	10.0
Example 23	B	20.0
Example 24	E	15.0
Example 25	F	15.0
Comparative Example 6	B	10.0
Comparative Example 7	C	10.0
Comparative Example 8	D	10.0
Comparative Example 9	D	10.0
Comparative Example 10	B	10.0
Comparative Example 11	B	10.0
Comparative Example 12	B	10.0

Table 7 (continued)

Examples and Comparative Examples	Production of black magnetic acicular composite particles		
	Coat formation step with carbon black		
	Edge runner treatment		Amount adhered (calculated as C) (wt. %)
	Linear load (Kg/cm)	Time (min.)	
Example 13	45	30	9.02
Example 14	60	20	13.00
Example 15	60	20	4.72
Example 16	30	25	9.01
Example 17	60	20	13.01
Example 18	45	30	12.95
Example 19	60	20	8.99
Example 20	30	30	13.01
Example 21	30	30	6.91
Example 22	60	20	9.00
Example 23	45	30	16.45
Example 24	30	40	12.86
Example 25	60	30	12.99
Comparative Example 6	45	30	9.08
Comparative Example 7	60	30	9.00
Comparative Example 8	45	30	9.03
Comparative Example 9	60	30	9.02
Comparative Example 10	60	30	9.01
Comparative Example 11	60	30	9.00
Comparative Example 12	60	30	9.05

Table 8

Examples and Comparative Examples	Properties of black magnetic acicular composite particles		
	Average major axial diameter ( $\mu\text{m}$ )	Average minor axial diameter ( $\mu\text{m}$ )	Aspect ratio (-)
Example 13	0.278	0.0341	8.2:1
Example 14	0.279	0.0342	8.2:1
Example 15	0.213	0.0290	7.3:1
Example 16	0.293	0.0364	8.0:1
Example 17	0.154	0.0230	6.7:1
Example 18	0.131	0.0185	7.1:1
Example 19	0.279	0.0342	8.2:1
Example 20	0.215	0.0294	7.3:1
Example 21	0.295	0.0367	8.0:1
Example 22	0.152	0.0225	6.8:1
Example 23	0.133	0.0188	7.1:1
Example 24	0.277	0.0343	8.1:1
Example 25	0.277	0.0342	8.1:1
Comparative Example 6	0.274	0.0336	8.2:1
Comparative Example 7	0.274	0.0336	8.2:1
Comparative Example 8	0.276	0.0340	8.1:1
Comparative Example 9	0.274	0.0336	8.2:1
Comparative Example 10	0.274	0.0336	8.2:1
Comparative Example 11	0.274	0.0336	8.2:1
Comparative Example 12	0.275	0.0338	8.1:1

Table 8 (continued)

Examples and Comparative Examples	Properties of black magnetic acicular composite particles		
	Geometrical standard deviation value (-)	BET specific surface area value (m <sup>2</sup> /g)	Coercive force value (Oe)
Example 13	1.37	43.5	675
Example 14	1.41	40.2	659
Example 15	1.35	44.3	830
Example 16	1.43	34.2	694
Example 17	1.44	59.0	876
Example 18	1.40	58.1	1,893
Example 19	1.39	41.7	652
Example 20	1.37	45.2	817
Example 21	1.42	35.6	680
Example 22	1.44	57.0	878
Example 23	1.40	59.9	1,881
Example 24	1.39	40.5	667
Example 25	1.40	43.4	665
Comparative Example 6	-	45.6	668
Comparative Example 7	-	44.8	669
Comparative Example 8	-	46.3	666
Comparative Example 9	-	45.2	668
Comparative Example 10	-	42.3	670
Comparative Example 11	-	42.2	670
Comparative Example 12	-	41.6	671

Table 8 (continued)

Examples and Comparative Examples	Properties of black magnetic acicular composite particles		
	Saturation magnetization value (emu/g)	Volume resistivity value ( $\cdot\cdot\text{cm}$ )	Blackness ( $I^*$ value) (-)
Example 13	77.4	$2.1 \times 10^4$	18.6
Example 14	70.1	$5.1 \times 10^3$	18.4
Example 15	73.2	$6.5 \times 10^4$	18.5
Example 16	79.4	$8.3 \times 10^4$	19.1
Example 17	84.8	$5.9 \times 10^4$	18.5
Example 18	130.6	$2.9 \times 10^4$	18.2
Example 19	69.5	$7.3 \times 10^3$	18.8
Example 20	72.9	$9.9 \times 10^3$	18.9
Example 21	76.8	$6.6 \times 10^4$	18.2
Example 22	75.9	$8.8 \times 10^3$	19.1
Example 23	129.3	$4.1 \times 10^4$	18.7
Example 24	71.1	$3.2 \times 10^3$	19.1
Example 25	70.8	$2.4 \times 10^3$	19.3
Comparative Example 6	70.6	$6.8 \times 10^6$	21.8
Comparative Example 7	70.3	$6.6 \times 10^6$	22.0
Comparative Example 8	70.1	$2.2 \times 10^6$	19.0
Comparative Example 9	70.3	$7.6 \times 10^6$	22.0
Comparative Example 10	69.8	$3.3 \times 10^4$	19.3
Comparative Example 11	69.9	$3.1 \times 10^4$	19.2
Comparative Example 12	70.1	$1.2 \times 10^4$	19.0



Table 8 (continued)

Examples and Comparative Examples	Properties of black magnetic acicular composite particles	
	Myristic acid adsorption (mg/m <sup>2</sup> )	Carbon black desorption percentage (%)
Example 13	0.27	7.6
Example 14	0.24	6.9
Example 15	0.24	7.2
Example 16	0.27	7.9
Example 17	0.24	7.0
Example 18	0.27	6.7
Example 19	0.21	3.9
Example 20	0.23	3.8
Example 21	0.23	3.4
Example 22	0.22	3.6
Example 23	0.24	4.4
Example 24	0.29	9.2
Example 25	0.28	9.3
Comparative Example 6	0.33	30.4
Comparative Example 7	0.34	24.2
Comparative Example 8	0.38	21.8
Comparative Example 9	0.44	26.3
Comparative Example 10	0.46	51.8
Comparative Example 11	0.42	37.5
Comparative Example 12	0.39	21.0

Table 9

Kind of non-magnetic particles	Properties of non-magnetic particles for non-magnetic undercoat layer	
	Kind	Particle shape
Non-magnetic particles 1	Hematite particles	Spindle-shaped
Non-magnetic particles 2	Goethite particles	Acicular
Non-magnetic particles 3	Hematite particles	Acicular
Non-magnetic particles 4	Hematite particles	Acicular
Non-magnetic particles 5	Hematite particles	Acicular
Non-magnetic particles 6	Goethite particles	Acicular

Table 9 (continued)

Kind of non-magnetic particles	Properties of non-magnetic particles for non-magnetic undercoat layer		
	Average major axial diameter ( $\mu\text{m}$ )	Average minor axial diameter ( $\mu\text{m}$ )	Aspect ratio (-)
Non-magnetic particles 1	0.187	0.0240	7.8:1
Non-magnetic particles 2	0.240	0.0272	8.8:1
Non-magnetic particles 3	0.143	0.0210	6.8:1
Non-magnetic particles 4	0.115	0.0179	6.4:1
Non-magnetic particles 5	0.143	0.0211	6.8:1
Non-magnetic particles 6	0.240	0.0273	8.8:1

Table 9 (continued)

Kind of non-magnetic particles	Properties of non-magnetic particles for non-magnetic undercoat layer	
	Geometrical standard deviation value (-)	BET specific surface area value (m <sup>2</sup> /g)
Non-magnetic particles 1	1.33	43.3
Non-magnetic particles 2	1.37	86.3
Non-magnetic particles 3	1.37	54.9
Non-magnetic particles 4	1.35	58.3
Non-magnetic particles 5	1.37	55.6
Non-magnetic particles 6	1.35	88.1

Table 9 (continued)

Kind of non-magnetic particles	Properties of non-magnetic particles for non-magnetic undercoat layer		
	Coating amount of Al (wt. %)	Al content (wt. %)	Amount of carbon black adhered (calculated as C) (wt. %)
Non-magnetic particles 1	-	-	-
Non-magnetic particles 2	-	-	-
Non-magnetic particles 3	0.98	-	-
Non-magnetic particles 4	-	0.67	-
Non-magnetic particles 5	-	-	4.75
Non-magnetic particles 6	-	-	4.81

Table 9 (continued)

Kind of non-magnetic particles	Properties of non-magnetic particles for non-magnetic undercoat layer	
	Volume resistivity value ( $\bullet\bullet$ cm)	Blackness (L* value) (-)
Non-magnetic particles 1	$8.6 \times 10^8$	32.6
Non-magnetic particles 2	$9.6 \times 10^7$	34.6
Non-magnetic particles 3	$4.6 \times 10^8$	28.4
Non-magnetic particles 4	$3.2 \times 10^8$	29.6
Non-magnetic particles 5	$3.6 \times 10^4$	18.5
Non-magnetic particles 6	$5.8 \times 10^3$	20.3

Table 10

Undercoat layer	Production of non-magnetic undercoat layer		Properties of coating composition
	Kind of non- magnetic particles	Weight ratio of particles to resin (-)	Viscosity (cP)
Undercoat layer 1	Non-magnetic particles 1	5.0:1	310
Undercoat layer 2	Non-magnetic particles 2	5.0:1	1,139
Undercoat layer 3	Non-magnetic particles 3	5.0:1	448
Undercoat layer 4	Non-magnetic particles 4	5.0:1	403
Undercoat layer 5	Non-magnetic particles 5	5.0:1	399
Undercoat layer 6	Non-magnetic particles 6	5.0:1	1,336

Table 10 (continued)

Undercoat layer	Properties of non-magnetic undercoat layer		
	Thickness ( $\mu\text{m}$ )	Gloss (%)	Surface roughness Ra (nm)
Undercoat layer 1	3.4	193	8.2
Undercoat layer 2	3.5	180	12.0
Undercoat layer 3	3.4	205	6.3
Undercoat layer 4	3.4	211	6.2
Undercoat layer 5	3.4	199	7.1
Undercoat layer 6	3.5	185	9.0



Table 10 (continued)

Undercoat layer	Properties of non-magnetic undercoat layer		
	Young's modulus (relative value)	Linear absorption ( $\mu\text{m}^{-1}$ )	Surface electrical resistivity value ( $\bullet/\text{cm}^2$ )
Undercoat layer 1	123	1.01	$1.1 \times 10^{14}$
Undercoat layer 2	125	0.79	$2.1 \times 10^{13}$
Undercoat layer 3	126	1.01	$3.5 \times 10^{13}$
Undercoat layer 4	125	0.98	$3.6 \times 10^{13}$
Undercoat layer 5	125	1.52	$4.1 \times 10^9$
Undercoat layer 6	129	1.46	$2.3 \times 10^{10}$

Table 11

Examples	Production of magnetic recording medium		Properties of coating composition
	Kind of non-magnetic undercoat layer	Kind of magnetic acicular particles	Viscosity (cP)
Example 26	Undercoat layer 1	Example 1	2,304
Example 27	Undercoat layer 2	Example 2	2,816
Example 28	Undercoat layer 3	Example 3	2,560
Example 29	Undercoat layer 4	Example 4	2,944
Example 30	Undercoat layer 5	Example 5	6,400
Example 31	Undercoat layer 6	Example 6	2,176
Example 32	Undercoat layer 1	Example 7	2,252
Example 33	Undercoat layer 2	Example 8	2,048
Example 34	Undercoat layer 3	Example 9	2,406
Example 35	Undercoat layer 4	Example 10	5,376
Example 36	Undercoat layer 5	Example 11	2,150
Example 37	Undercoat layer 6	Example 12	2,022

Table 11 (continued)

Examples	Properties of magnetic recording medium		
	Thickness of magnetic layer ( $\mu\text{m}$ )	Coercive force value (Oe)	Squareness (Br/Bm) (-)
Example 26	1.0	741	0.88
Example 27	1.0	903	0.89
Example 28	1.1	768	0.88
Example 29	1.0	966	0.88
Example 30	1.2	1,982	0.88
Example 31	1.0	743	0.89
Example 32	1.1	906	0.89
Example 33	1.1	770	0.90
Example 34	1.1	969	0.90
Example 35	1.1	1,983	0.89
Example 36	1.0	745	0.88
Example 37	1.0	748	0.88

Table 11 (continued)

Examples	Properties of magnetic recording medium		
	Gloss (%)	Surface roughness Ra (nm)	Young's modulus (relative value)
Example 26	196	6.3	138
Example 27	188	7.1	141
Example 28	210	6.1	143
Example 29	214	6.4	141
Example 30	234	6.0	140
Example 31	198	6.0	142
Example 32	189	6.4	141
Example 33	213	5.8	142
Example 34	217	5.7	145
Example 35	235	5.6	142
Example 36	201	6.6	143
Example 37	193	6.8	145

Table 11 (continued)

Examples	Properties of magnetic recording medium		
	Linear absorption ( $\mu\text{m}^{-1}$ )	Running durability (min.)	Surface electrical resistivity value ( $\cdot/\text{cm}^2$ )
Example 26	1.54	26.9	$6.6 \times 10^7$
Example 27	1.51	27.3	$8.3 \times 10^7$
Example 28	1.51	27.1	$9.3 \times 10^7$
Example 29	1.55	27.3	$1.8 \times 10^7$
Example 30	1.65	26.4	$2.3 \times 10^7$
Example 31	1.71	29.8	$5.4 \times 10^7$
Example 32	1.56	28.9	$5.8 \times 10^7$
Example 33	1.58	29.3	$2.3 \times 10^7$
Example 34	1.61	27.8	$8.8 \times 10^7$
Example 35	1.66	28.8	$9.3 \times 10^7$
Example 36	1.67	26.1	$2.3 \times 10^7$
Example 37	1.66	25.8	$1.6 \times 10^7$

Table 12

Examples	Production of magnetic recording medium		Properties of coating composition
	Kind of non-magnetic undercoat layer	Kind of magnetic acicular particles	Viscosity (cP)
Example 38	Undercoat layer 1	Example 13	2,560
Example 39	Undercoat layer 1	Example 14	2,184
Example 40	Undercoat layer 2	Example 15	2,406
Example 41	Undercoat layer 3	Example 16	2,150
Example 42	Undercoat layer 4	Example 17	2,560
Example 43	Undercoat layer 5	Example 18	3,844
Example 44	Undercoat layer 6	Example 19	2,022
Example 45	Undercoat layer 1	Example 20	2,048
Example 46	Undercoat layer 2	Example 21	2,150
Example 47	Undercoat layer 3	Example 22	1,864
Example 48	Undercoat layer 4	Example 23	3,844
Example 49	Undercoat layer 5	Example 24	1,840
Example 50	Undercoat layer 6	Example 25	1,768

Table 12 (continued)

Examples	Properties of magnetic recording medium		
	Thickness of magnetic layer ( $\mu\text{m}$ )	Coercive force value (Oe)	Squareness (Br/Bm) (-)
Example 38	1.1	739	0.88
Example 39	1.0	743	0.88
Example 40	1.0	902	0.88
Example 41	1.0	765	0.89
Example 42	1.0	959	0.89
Example 43	1.1	1,980	0.88
Example 44	1.1	747	0.89
Example 45	1.0	913	0.90
Example 46	1.0	781	0.91
Example 47	1.0	966	0.89
Example 48	1.1	1,980	0.90
Example 49	1.0	743	0.89
Example 50	1.0	750	0.89

Table 12 (continued)

Examples	Properties of magnetic recording medium		
	Gloss (%)	Surface roughness Ra (nm)	Young's modulus (relative value)
Example 38	196	6.2	138
Example 39	193	6.1	139
Example 40	191	6.9	140
Example 41	213	6.2	141
Example 42	214	6.4	143
Example 43	236	5.9	141
Example 44	195	5.8	143
Example 45	193	6.1	142
Example 46	215	5.6	143
Example 47	219	5.6	146
Example 48	238	5.6	146
Example 49	203	6.5	143
Example 50	196	6.6	143



Table 12 (continued)

Examples	Properties of magnetic recording medium	
	Linear absorption ( $\mu\text{m}^{-1}$ )	Friction coefficient (-)
Example 38	2.89	0.28
Example 39	2.91	0.27
Example 40	2.82	0.26
Example 41	2.86	0.26
Example 42	2.88	0.28
Example 43	3.21	0.28
Example 44	3.03	0.23
Example 45	2.91	0.24
Example 46	2.80	0.22
Example 47	2.92	0.21
Example 48	2.89	0.24
Example 49	3.01	0.30
Example 50	2.99	0.29

Table 12 (continued)

Examples	Properties of magnetic recording medium	
	Running durability (min.)	Surface electrical resistivity value ( $\bullet/\text{cm}^2$ )
Example 38	•30	$4.1 \times 10^6$
Example 39	28.9	$1.8 \times 10^6$
Example 40	28.6	$3.1 \times 10^6$
Example 41	28.0	$6.3 \times 10^6$
Example 42	•30	$1.3 \times 10^6$
Example 43	27.9	$6.8 \times 10^5$
Example 44	•30	$7.5 \times 10^5$
Example 45	•30	$2.3 \times 10^6$
Example 46	•30	$4.1 \times 10^6$
Example 47	•30	$9.8 \times 10^5$
Example 48	•30	$1.2 \times 10^6$
Example 49	27.1	$5.5 \times 10^5$
Example 50	26.5	$4.0 \times 10^5$

Table 13

Comparative Examples	Production of magnetic recording medium		Properties of coating composition Viscosity (cP)
	Kind of non- magnetic undercoat layer	Kind of magnetic particles	
Comparative Example 13	Undercoat layer 1	Core particles 1	3,218
Comparative Example 14	Undercoat layer 1	Core particles 2	2,813
Comparative Example 15	Undercoat layer 1	Core particles 3	3,384
Comparative Example 16	Undercoat layer 1	Core particles 4	2,813
Comparative Example 17	Undercoat layer 1	Core particles 5	10,240
Comparative Example 18	Undercoat layer 1	Comparative Example 1	3,813
Comparative Example 19	Undercoat layer 1	Comparative Example 2	3,618
Comparative Example 20	Undercoat layer 1	Comparative Example 3	3,532
Comparative Example 21	Undercoat layer 1	Comparative Example 4	3,653
Comparative Example 22	Undercoat layer 1	Comparative Example 5	4,210
Comparative Example 23	Undercoat layer 1	Comparative Example 6	3,402
Comparative Example 24	Undercoat layer 1	Comparative Example 7	3,821
Comparative Example 25	Undercoat layer 1	Comparative Example 8	3,836
Comparative Example 26	Undercoat layer 1	Comparative Example 9	3,306
Comparative Example 27	Undercoat layer 1	Comparative Example 10	3,413
Comparative Example 28	Undercoat layer 1	Comparative Example 11	3,526
Comparative Example 29	Undercoat layer 1	Comparative Example 12	3,600

Table 13 (continued)

Comparative Examples	Properties of magnetic recording medium		
	Thickness of magnetic layer ( $\mu\text{m}$ )	Coercive force value (Oe)	Squareness (Br/Bm) (-)
Comparative Example 13	1.0	738	0.84
Comparative Example 14	1.0	883	0.83
Comparative Example 15	1.0	742	0.83
Comparative Example 16	1.0	946	0.80
Comparative Example 17	1.2	1,960	0.85
Comparative Example 18	1.0	731	0.82
Comparative Example 19	1.0	736	0.84
Comparative Example 20	1.0	738	0.83
Comparative Example 21	1.1	741	0.85
Comparative Example 22	1.0	736	0.80
Comparative Example 23	1.0	733	0.82
Comparative Example 24	1.0	728	0.81
Comparative Example 25	1.1	736	0.83
Comparative Example 26	1.0	746	0.81
Comparative Example 27	1.1	723	0.83
Comparative Example 28	1.0	736	0.84
Comparative Example 29	1.0	735	0.84

Table 13 (continued)

Comparative Examples	Properties of magnetic recording medium		
	Gloss (%)	Surface roughness Ra (nm)	Young's modulus (relative value)
Comparative Example 13	164	10.2	127
Comparative Example 14	171	10.2	128
Comparative Example 15	168	10.6	128
Comparative Example 16	160	11.1	127
Comparative Example 17	196	13.0	126
Comparative Example 18	163	18.4	128
Comparative Example 19	168	17.3	128
Comparative Example 20	169	16.4	128
Comparative Example 21	163	21.3	128
Comparative Example 22	160	21.6	126
Comparative Example 23	164	15.5	127
Comparative Example 24	165	19.6	127
Comparative Example 25	168	15.2	128
Comparative Example 26	163	15.6	128
Comparative Example 27	160	18.9	128
Comparative Example 28	162	20.1	128
Comparative Example 29	169	14.6	128

Table 13 (continued)

Comparative Examples	Properties of magnetic recording medium	
	Linear absorption ( $\mu\text{m}^{-1}$ )	Friction coefficient (-)
Comparative Example 13	1.06	0.44
Comparative Example 14	1.08	0.43
Comparative Example 15	1.11	0.43
Comparative Example 16	1.07	0.42
Comparative Example 17	1.19	0.51
Comparative Example 18	1.16	0.46
Comparative Example 19	1.18	0.43
Comparative Example 20	1.19	0.42
Comparative Example 21	1.20	0.45
Comparative Example 22	1.20	0.46
Comparative Example 23	1.75	0.41
Comparative Example 24	1.76	0.43
Comparative Example 25	1.78	0.46
Comparative Example 26	1.79	0.48
Comparative Example 27	1.79	0.43
Comparative Example 28	1.76	0.41
Comparative Example 29	1.76	0.46

Table 13 (continued)

Comparative Examples	Properties of magnetic recording medium	
	Running durability (min.)	Surface electrical resistivity value ( $\cdot/\text{cm}^2$ )
Comparative Example 13	19.2	$4.8 \times 10^{12}$
Comparative Example 14	18.6	$7.4 \times 10^{12}$
Comparative Example 15	18.0	$7.3 \times 10^{11}$
Comparative Example 16	19.1	$1.4 \times 10^{11}$
Comparative Example 17	17.2	$1.8 \times 10^{11}$
Comparative Example 18	9.6	$5.8 \times 10^{11}$
Comparative Example 19	8.3	$3.2 \times 10^{11}$
Comparative Example 20	6.4	$1.1 \times 10^{11}$
Comparative Example 21	5.8	$2.6 \times 10^{11}$
Comparative Example 22	6.1	$8.6 \times 10^{10}$
Comparative Example 23	10.5	$7.6 \times 10^8$
Comparative Example 24	11.1	$5.8 \times 10^8$
Comparative Example 25	13.1	$3.1 \times 10^8$
Comparative Example 26	11.4	$4.8 \times 10^8$
Comparative Example 27	15.1	$5.1 \times 10^8$
Comparative Example 28	16.2	$4.6 \times 10^8$
Comparative Example 29	16.6	$2.9 \times 10^8$

EFFECT OF THE PRESENT INVENTION

In the magnetic recording medium of the present invention, the non-magnetic undercoat layer is formed, and the black magnetic acicular composite particles having an excellent blackness and a low volume resistivity value are used as magnetic particles therefor. Therefore, the obtained magnetic recording medium can exhibit a small light transmittance and a low surface electrical resistivity value. Further, since the amount of carbon black fine particles incorporated into the magnetic recording layer is reduced to as small a level as possible and the black magnetic acicular composite particles themselves are enhanced in dispersibility in vehicle, the obtained magnetic recording medium can exhibit a smooth surface. Accordingly, the magnetic recording medium of the present invention is suitable as those for high-density recording.

By using the above black magnetic acicular composite particles adhering carbon black in a large amount and having a controlled myristic acid-adsorption, the magnetic recording medium according to the present invention can exhibit not only the above-mentioned properties, but also a small friction coefficient and an excellent running durability. Therefore, the magnetic recording medium of the present invention is suitable as those for high-density recording.